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ERRATA.

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Pag.	Line
ii, 532	13 ⁴) for "tungstate" read "molybdate,"
"	12 ⁴)
"	11 ⁴)
"	10 ⁴) .. "molybdate" .. "tungstate."
"	9 ⁴)

VOL. CVI (ABSTR., 1914).

i, 97 12 for "Content" read "Constants."

* From bottom.

DIBROMIDES OF THE TYPE OF ETHYLENE DIBROMIDE, ETC. 2301

3·2 grams of trimethylene glycol were obtained, representing a yield of 80 per cent. of the theoretical.

Propylene Glycol Diacetate.

0·1 Gram of sodium was dissolved in 25 c.c. of absolute alcohol, and the solution heated on a steam-bath with 8·0 grams of propylene glycol diacetate for twelve hours. On distillation, the product (6·0 grams) consisted largely of unchanged diacetate, boiling at 183–186°. As the boiling point of propylene glycol is only 3° higher than this, it is possible that the product contained a little of the glycol. It was, however, a mobile liquid, and completely miscible with ether. Propylene glycol is very viscous, and is insoluble in ether.

αγ-Butylene Glycol Diacetate.

0·1 Gram of sodium was dissolved in 25 c.c. of absolute alcohol, and the solution boiled on a steam-bath with 8·7 grams of αγ-butylene glycol diacetate for eight hours. On distillation, a product (5 grams) was obtained, boiling at 198°, which was insoluble in water and completely soluble in ether. It was concluded to be the unchanged diacetate. An experiment on a larger scale, using one molecular proportion of sodium ethoxide, gave 60 per cent. of the theoretical amount of αγ-butylene glycol.

ψ-Butylene Glycol Diacetate.

0·1 Gram of sodium was dissolved in 25 c.c. of absolute alcohol, and the solution boiled with 8·7 grams of ψ-butylene glycol diacetate for eight hours. The product consisted of unchanged diacetate, boiling at 188–190°. It was soluble in ether and insoluble in water.

The general method of preparing glycols mentioned on p. 2296 was carried out as follows. 1·15 Grams of sodium were dissolved in 25 c.c. of absolute alcohol containing about 1 per cent. of water, the ester was added, and the mixture was heated for about an hour on a steam-bath in a reflux apparatus. The supernatant liquid was evaporated, and the residue was boiled for about fifteen minutes with 2·3 c.c. of water, and then saturated with carbon dioxide to remove any excess of alkali. The mass was then distilled, and the distillate fractionated. The yield varied from 60 to 85 per cent. of the theoretical.

Ethyleneglycol diacetato	gave	85	per cent.
Propylene "	"	76	"
Trimethylene "	"	63	"
αγ-Butylene "	"	60	"

On classifying the acetates investigated, it will be seen that they fall into two distinct classes, according to their behaviour with alcoholic sodium ethoxide: (1) those which are hydrolysed by this means, namely, ethylene glycol diacetate, trimethylene glycol diacetate, and α -butylene glycol diacetate; and (2) those which are not hydrolysed, namely, β -butylene glycol diacetate and propylene glycol diacetate. It will be noticed that class 2 (except the first) have their acetoxy groups attached to adjacent carbon atoms, whilst class 1 have them attached to carbon atoms which are not adjacent.

In conclusion, the author desires to acknowledge his indebtedness to the Research Fund Committee of the Chemical Society for a grant which has partly covered the expenses of this research, and also to thank Prof. A. Lapworth and Mr. E. Hope for their advice and encouragement.

MOSLEY RESEARCH LABORATORIES,
THE UNIVERSITY, MANCHESTER.

CCXIII.—*Electromotive Forces in Alcohol. Part IV.
Combinations of the Hydrogen and Calomel
Electrodes.*

By REGINALD FURNESS, ROBERT TAYLOR HARDMAN, and
EDGAR NEWBERY.

The investigations described in the earlier papers of this series (T., 1911, **99**, 1417, 2242; 1912, **101**, 2249) have been continued in the hope that it might ultimately prove possible to compare by electrometric methods the thermodynamic potentials of highly dilute hydrogen chloride in water and alcohol respectively. Progress in this direction was only possible after further examination of: (a) the behaviour of the calomel electrode in alcoholic solutions of mineral chlorides; (b) the influence of metallic chlorides on the potential of the hydrogen electrode in alcohol; and (c) the potential differences between electrodes reversible to chloridion and hydronium respectively in alcoholic solution. At Professor Lapworth's suggestion, the authors have therefore undertaken the present investigation, measured the potential differences in question, submitted the results to a careful theoretical analysis, and thus defined certain lines along which definite progress may be hoped for.

EXPERIMENTAL.

[REGINALD FURNESS and ROBERT TAYLOR HARDMAN.]

The alcohol used in the following experiments was dried as described in Part I (*loc. cit.*, p. 1420), and further purified from all traces of ammonia by redistillation after it had been rendered faintly acid to methyl-orange by addition of a highly dilute solution of hydrogen chloride in anhydrous alcohol, every precaution being taken to prevent access of moisture during this and all subsequent processes.

All measurements were made with a very carefully calibrated potentiometer, made by the Land and Seekabelwerke, in connexion with a very sensitive galvanometer, by Gambrell Bros., as null instrument.

The calomel cells were similar to those figured in Part I, but were provided with a wide side-tube, which greatly increased the sensitiveness of the combinations, and this side-tube was connected with that of the hydrogen electrode-cell by means of rubber tubing. In these experiments the danger of intermixing of the cell-liquids was practically non-existent, an advantage which obviated many of the manipulative difficulties previously met with when employing combinations of two hydrogen electrodes.

The hydrogen electrode cells were the same as those employed by Wilsmore and figured on p. 239 of Lehfeldt's "Electrochemistry" (Text Books of Physical Chemistry, 1904, Longmans, Green and Co.). They were wholly constructed of glass, however, and thin platinum foil was used as electrode throughout.

The whole combination of hydrogen with calomel electrode, with the exception of the junction of the side-tubes and a small upper portion of each cell, was immersed in the water of a thermostat kept at $25 \pm 0.02^\circ$.

In all cases where sensibly constant electromotive forces were not observed, or where constancy was not attained within fifteen minutes from the time of setting up the combination, the hydrogen electrode cell was refilled, relifted with newly platinised electrodes, and readings were begun *ab initio*.

Where measurements were made with saturated solutions of sodium chloride, complete saturation of the alcohol with the salt was ensured by adding a large excess of the powdered anhydrous salt in the electrode cell itself; it was found that in these circumstances the potential difference of a pair of calomel electrodes reached a steady value in about two hours after setting up, and remained constant for an indefinite period.

The standard of comparison was a Weston cell of the most

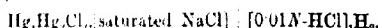
recent type, supplied by the Cambridge Scientific Instrument Company.

Results.

In the following summaries of results, the *E.M.F.* quoted for each combination is the mean of six readings taken at intervals during two to three hours, the first having taken about fifteen minutes after the combination had been set up. In no case did the observed *E.M.F.* vary by more than one millivolt for any single combination.

The arrows represent the directions of the currents within the cells.

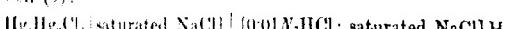
Cell (a):



Mean *E.M.F.* for different combinations in millivolts: 253.3, 253.0, 253.0, 253.7, 254.0.

Mean *E.M.F.* of five combinations = 0.2534 volt.

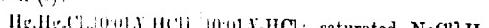
Cell (b):



Mean *E.M.F.* for different combinations in millivolts: 247.5, 248.0, 248.0, 248.3, 249.0, 248.0.

Mean *E.M.F.* of seven combinations = 0.2482 volt.

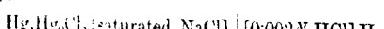
Cell (c):



Mean *E.M.F.* for different combinations in millivolts: 248.7, 248.9, 248.6, 248.0.

Mean *E.M.F.* of four combinations = 0.2483 volt.

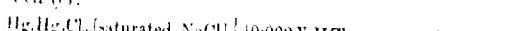
Cell (d):



Mean *E.M.F.* for different combinations in millivolts: 282.6, 280.3, 281.0, 280.0, 280.0, 278.0, 281.0.

Mean *E.M.F.* of seven combinations = 0.2804 volt.

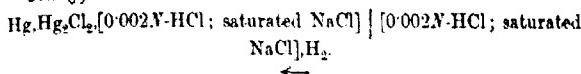
Cell (e):



Mean *E.M.F.* of different combinations in millivolts: 279.2, 279.6, 279.3, 280.4.

Mean E.M.F. of five combinations = 0.2795 volt.

Cell (*f*):



Mean *E.M.F.* for different combinations in millivolts: 284.0, 284.0, 283.7, 282.6.

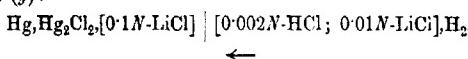
Mean E.M.F. of four combinations = 0.2836 volt.

Several measurements were also carried out in which lithium chloride instead of sodium chloride was used.

Lithium chloride was employed by Hardman and Lapworth for the purpose of minimising liquid contact-potential differences in their experiments with the hydrogen electrode (Parts II and III, *loc. cit.*), and the authors have therefore examined the following combinations in order to exclude the possible suggestion that this salt may have any unforeseen and important influence on the potential of the hydrogen electrode in alcoholic solutions of hydrogen chloride.

The general remarks already made as to the methods and apparatus used in the experiments with sodium chloride also apply to the cases below.

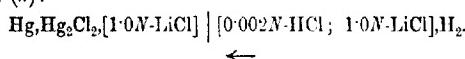
Cell (*g*):



E.M.F. for different combinations in millivolts: 260, 259, 260.

Mean E.M.F. for three combinations = 0.2595 volt.

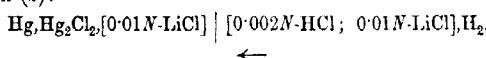
Cell (*h*):



E.M.F. of different combinations in millivolts: 249, 246, 247.

Mean E.M.F. of three combinations = 0.2473 volt.

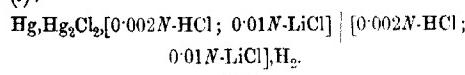
Cell (*k*):



E.M.F. of different combinations in millivolts: 282, 283, 284.

Mean E.M.F. of three combinations = 0.283 volt.

Cell (*l*):



E.M.F. of different combinations in millivolts: 259·4, 259·8.

Mean E.M.F. of two combinations=0·2596 volt.

It may be added that the influence of small quantities of moisture in the hydrogen electrode compartment of some of the above combinations was examined. The potential differences increased to a marked extent in accordance with the results already obtained by Hardman and Lapworth in working with combinations of two hydrogen electrodes.

Analysis of the foregoing determinations of electromotive forces.

[EDGAR NEWBERY.]

The above measurements will be required for the calculation of the differences in the thermodynamic potentials of dilute solutions of hydrogen chloride in alcohol and water respectively, utilising certain novel data, which will be given in future communications.

Having regard, however, to the uncertainty which still attaches to measurements of potential differences in alcoholic solutions, it will be necessary, in the first instance, to ascertain whether these observations can be regarded as trustworthy from the point of view of agreement among themselves, so far as can be judged by the application of the standard methods of calculation to such cases.

In the following calculations it has been assumed that the relative mobilities of the ions, with the exception of the hydrogen ion, are the same as in water (compare Lapworth and Partington, T., 1911, 99, 1420), and that the transport number of the chloridion in alcoholic hydrogen chloride is 0·30. The possible error arising out of inaccuracy in the latter assumption affects the results of these calculations to an extent which is well within the other experimental errors at present attached to such determinations in alcoholic solution.

The relative mobilities assumed throughout are thus: Cl, 62; Na, 40·5; H, 145.

The differences between the electromotive forces of any two of the combinations described by Furness and Hardman have been calculated as in the following example:

*Theoretical Difference in Electromotive Force between the Cells
(a) and (b).*

The difference in the absolute potential of the mercury in cell combination (a) and that in (b) is given by Nernst's well-known formula

$$\frac{RT}{F} \log_e \frac{C_a'}{C_b'}$$

where C_a' and C_b' are the concentrations of the chloridion in the calomel electrodes of (a) and (b) respectively, R , T , and F having their usual significance.

Calculation of C_b' .— C_b' has been calculated with the aid of: (1) the equations given by Nernst ("Theoretical Chemistry," English Translation, 1904, p. 527) for the change in solubility of a binary electrolyte caused by the addition of another electrolyte having a common ion, and (2) an application of Arrhenius' theory of isohydric solutions.

The equations given by Nernst are:

$$m_o(1-a_o) = m(1-a) \dots \dots \dots \quad (\alpha)$$

$$(m_o a_o)^2 = ma(ma + x). \dots \dots \dots \quad (\beta)$$

where m_o and a_o are respectively the solubility and degree of ionisation of the electrolyte at saturation in the pure solvent, m and a the corresponding terms in the mixed solution, and x the concentration of the new ion appearing on addition of the second electrolyte.

In order to evaluate x , m , and a , it is necessary to apply the theory of isohydric solutions, and, in the first instance, on the assumption that the presence of the second electrolyte does not affect the solubility of the first; a rough value for x is thus obtained, which may be substituted in the equations α and β when first approximations to m and a are obtained. The law of isohydric solutions is then applied once more, and a new value for x obtained, the process being repeated until the value of x is unaltered by such repetition. The process is very lengthy, involves repeated references to the conductivity curves for sodium and hydrogen chlorides in alcohol (Völlmer, *Ann. Phys. Chem.*, 1894, *iii*, 52, 382, and Lapworth and Partington, T., 1911, 99, 1417), and cannot be given in detail here.

In the present instance, for the calomel electrode of the combination (b), $m_o=0.0094$,* $a_o=0.62$; the calculations outlined above give $x=0.0069$, $m=0.0069$, and $a=0.50$.

From these results, C_b' (the concentration of the chloridion in the calomel cell (b)) = $ma + x = 0.01035$. Similar calculations were performed with reference to the mixed solutions in cells (e) and (f), and a table showing all the data obtained for both of the mixed solutions used is given below:

Concentration of:	Cells (b) and (e).	Cells (e) and (f).
Sodium chloride	0.0069	0.0087
Hydrogen chloride	0.01	0.002
Sodium ions.....	0.00345	0.00505
Hydrogen ions.....	0.0069	0.00146
Chlorine ions	0.01035	0.00631

* All quantities are given in gram-molecules per litre.

Boundary potentials in the cells were next calculated, using the above data with the aid of Henderson's equation. The calculations are perfectly straightforward, and examples are unnecessary. The results are as follows:

Cell	(a)	(b)	(c)	(d)	(e)	(f)
	0.0190	0.0147	0.0	0.0147	0.0063	0.0 volt

In every case, the boundary potential acts in the same direction as the *E.M.F.* of the cell.

The difference in absolute electromotive force between various pairs of cells is easily calculated by means of the Nernst formula already quoted, and, knowing the difference in boundary potential, the total potential difference is obtained, and may be compared with the experimental results obtained by Furness and Hardman. This has been done in the following table:

Cells compared.	Difference of absolute potential.	Difference of boundary potential.	Total calculated potential difference.	Measured potential difference.
(a) and (b)	+ 0.0011 volt.	- 0.0043 volt.	- 0.003 volt	- 0.005 volt.
(b) (c)	- 0.0147 ..	0.0147 ..	- 0.029 ..	- 0.000 ..
(b) (d)	+ 0.0027 ..	0.0084 ..	- 0.006 ..	- 0.001 ..
(c) (d)	- 0.0028 ..	0.0063 ..	- 0.009 ..	+ 0.004 ..
(c) (e)	+ 0.0352 ..	0.0043 ..	+ 0.034 ..	+ 0.027 ..
(b) (e)	+ 0.0398 ..	- 0.0084 ..	+ 0.031 ..	+ 0.032 ..
(b) (f)	+ 0.0517 ..	- 0.0 ..	+ 0.052 ..	+ 0.036 ..

The observed potential difference between *a* and *b* is in fairly good agreement with the calculated difference, also that between (b) and (c).

The values for (d) and (e) show a less satisfactory agreement, and here, possibly, some experimental error is responsible. If the measured *E.M.F.* of (d) is increased by about 0.006 volt, good agreement is obtained with the calculated differences, not only between (d) and (e), but also between (a) and (d). The error is therefore probably in the measurement of the potential of cell (d).

No hypothesis of experimental error can account for the great discrepancies observed between calculated and measured potential differences when cells (c) and (f) are employed. These are entirely at variance with any of the other cell values and with each other, the discrepancies being the greater the stronger the acid present in the cell.

We are therefore forced to the important conclusion that calomel electrodes in acid-alcoholic solutions are untrustworthy.

In view of the fact that the potential of the calomel electrode in the acid-alcoholic solutions is always too high, and also that this increase is greater with the stronger acid, it seems probable that these discrepancies have their origin in irreversible chemical

changes which occur when calomel is left in contact with alcoholic hydrogen chloride, for Lapworth and Partington have drawn attention to the fact that blackening of the calomel takes place under these conditions (T., 1911, **99**, 1422), although Furness and Hardman did not observe any such blackening in this case.

Possibly the weaker acids may not show this effect, but as the foregoing data render it probable that an error of 13 millivolts is caused by a $N/500$ -solution of hydrogen chloride, it would be unsafe to rely on measurements with the calomel electrode even in these without further experimental evidence. We may conclude, therefore:

- (1) That Furness and Hardman's numbers for the *E.M.F.* of cells (a), (b), and (c) are nearly correct, but that their number for the *E.M.F.* of cell (d) is probably too low by about 6 millivolts.*
- (2) That the calomel electrode does not give trustworthy results in acid-alcoholic solutions, but behaves satisfactorily in dilute alcoholic solutions of sodium chloride.

The authors desire to state that in the experiments described in the present paper much of the expense was defrayed from a grant from the Chemical Society received by one of them, and that they also had the advantage of using a certain amount of glass apparatus which had been purchased out of a grant to Professor Lapworth from the Government Grant Research Fund of the Royal Society.

CHEMICAL LABORATORIES,
UNIVERSITY OF MANCHESTER.

* This result, obtained with $N/500$ hydrogen chloride, although possibly exaggerated slightly by the uncertainties attaching to calculations based on the application of the gas laws to solutions of strong electrolytes, is a very interesting one when considered in connexion with the results of Hardman and Lapworth (Part II., T., 1912, **101**, 2251), who found that with increasing dilution of hydrogen chloride in alcohol, up to $N/100$, there appeared a growing discrepancy between the observed and calculated electromotive forces. It is now nearly certain that the transport number of hydron in alcoholic hydrogen chloride is not less than 0.3 and it would therefore appear that the performance of the hydrogen electrode here is satisfactory only when the conductivity of the solution is sufficiently great and that in alcoholic solutions of hydrogen chloride at $N/100$ to $N/500$, the absolute potential of the electrode appears about 3 to 6 millivolts too low.—A. LAPWORTH.

CCXIV.—*The Dissociation of Gaseous Nitrogen Trioxide.*

By BERNARD MOUAT JONES.

In 1907 Professor and Mrs. Baker showed (T., 91, 1862) that liquid nitrogen trioxide which had been carefully dried gave a vapour the density of which varied, according to the time of drying of the apparatus and the liquid, from 38·1 to 62·2. The theoretical value for pure N_2O_3 is 38, and for N_4O_6 76. The pressures under which the determinations were made were, with two exceptions, the atmospheric pressures, and the temperatures varied from 16° to 60°. It was concluded that gaseous nitrogen trioxide consisted of a mixture of N_4O_6 and N_2O_3 molecules, and that small traces of moisture promoted the dissociation of the higher polymeride into the simple N_2O_3 molecules; it was evident also that the amount of dissociation depended partly, at least, on the amount of moisture present. This conclusion was supported by the facts that the boiling point of liquid nitrogen trioxide is raised from -2° to +43°, and the colour of the liquid changes from green to blue by prolonged drying over phosphoric oxide (Baker, T., 1912, 101, 2339).

It is, however, a noteworthy fact that the vapour of nitrogen trioxide, even when very dry, is of a reddish-brown colour, indistinguishable in appearance, indeed, from that of N_2O_4 dissociating into NO_2 , and, on heating, the colour becomes darker in a way exactly similar to the behaviour of nitrogen peroxide. It appeared to the present author that this was a matter worth investigation, and that it was likely that Baker's gaseous nitrogen trioxide was not just a mixture of N_4O_6 and N_2O_3 , but a mixture of N_4O_6 (and possibly N_2O_3) with NO_2 and NO .

The simplest supposition appeared to be that the gas was a dissociating mixture represented by the equations



and that the effect of prolonged drying was to diminish the dissociation of the N_4O_6 molecules, the vapour density of the whole eventually approximating to that of pure N_4O_6 (which would appear to be colourless, or nearly colourless, in the gaseous state).

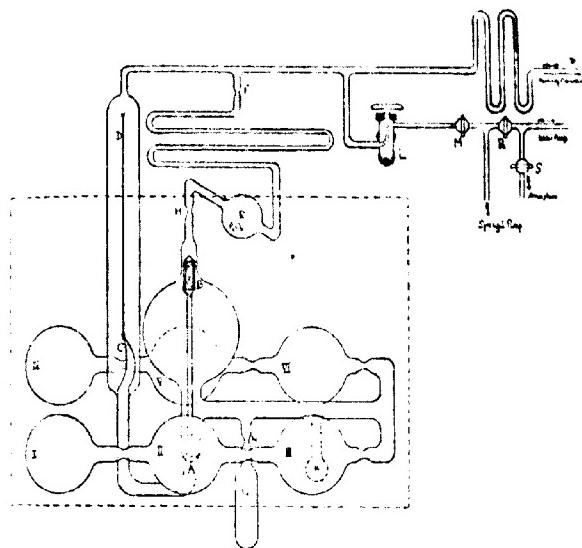
The object of the work now communicated was to test this supposition by determining the vapour densities of dried nitrogen trioxide at a series of temperatures, pressures, and volumes, which would provide the necessary data. It may be said here that the experimental results do not accord with this supposition, but they

indicate that a somewhat more complicated state of affairs really obtains, and they seem to be of sufficient interest to be worth recording.

EXPERIMENTAL.

The apparatus employed is shown in Fig. 1. The specimen of nitrogen trioxide used, which had been prepared and dried for two years by Professor Baker, was contained in a thin glass bulb, *A*, which could be broken when required by raising with a magnet a glass rod to which was attached a sealed tube containing a piece

FIG. 1.



of soft iron, *B*, and allowing it to fall. The apparatus consisted of six bulbs, *I*—*VI*, varying in size from about 92 c.c. to 185 c.c., sealed to each other and to the rest of the apparatus by thick-walled, narrow-boro (2–3 mm.) tubes. The tube *G* contained charcoal, and could be sealed off at *N*; the bulb *K* could be immersed in liquid air when required. The pressure inside the apparatus was determined by means of the glass manometer *C*, of the kind described by Jackson (*T.*, 1911, **99**, 1066), to which was attached a glass pointer *D*, 33 cm. long, the motions of which

could be observed by means of a reading microscope with micrometer eye-piece. The gauge was sensitive to rather less than 0.5 mm. of mercury. The outer tube of the gauge was attached to the rest of the apparatus by way of *F* and *E*, to a mercury manometer *P*, and to a Sprengel pump and water-pump by way of the taps *L* and *M*. Communication with the atmosphere was obtainable through the taps *R* and *S*. The bulb *E* contained phosphoric oxide, and there were constrictions in the tubing at *F* and *H*.

The apparatus having been set up, the taps *L* and *M* were opened, and the whole was exhausted by the Sprengel pump. At the same time it was thoroughly heated all over as strongly as was safe by a free flame. It was allowed to remain for several days, and the exhaustion and heating were repeated several times to get rid, as far as possible, of occluded gases. In the meantime, the zero position of the manometer pointer was determined. The apparatus was then sealed at *F*, thus separating the outer tube of the gauge from the main body of the apparatus, which was then allowed to remain in order to dry thoroughly. The preliminary stage of the drying was accomplished by immersing the charcoal bulb, *G*, in liquid air for three hours, during which time the whole apparatus was heated as strongly as was safe, and then sealing off the bulb at *N*. The whole was then allowed to remain for three months to complete the drying by means of the phosphoric oxide in the bulb *E*. After this time the apparatus was sealed at *H*, and the part *HEF* removed. The portion of the apparatus *A* was then surrounded by a freezing mixture of ice and calcium chloride, and the bulb of nitrogen trioxide broken by means of the glass rod. On removing the freezing mixture, the liquid slowly evaporated, completely filling the apparatus with a reddish-brown gas, and at the same time air was allowed to enter the outer tube of the gauge by way of *S*, *R*, *M*, *L* at a rate sufficient to keep the pressures on either side of *C* nearly the same. Throughout the whole series of experiments the difference of pressure on the two sides of the gauge was never allowed to exceed 100 mm., in order to prevent any possible variation in the zero point of the gauge. At the end the zero point was again determined, and found not to have varied appreciably.

The main portion of the apparatus was then surrounded by a bath, indicated by the dotted line, which could be well stirred by bubbling air through it, the temperature of which was given by two thermometers graduated in fifths of a degree. For temperatures up to about 60° the bath contained water; for higher temperatures, up to about 138°, glycerol. The bath was of such

size that its temperature could easily be kept constant to about $\pm 1^\circ$ for periods of about twenty minutes by merely regulating the size of the flames.

The presence of the nitrogen trioxide vapour was then determined at a series of temperatures from about 15° to 138° by introducing into or removing small quantities of air from the outer tube of the gauge until the pointer stood at the zero point. By arranging that the pressure in the short tube *L.M* differed only slightly from the pressure between *L* and the rest of the apparatus, it was possible to do this very readily and with considerable accuracy. At least three determinations were made at each temperature, and the values, as read on the manometer *P*, rarely varied by more than 0.5 mm. The height of the barometer and the temperature of the air were read at the same time.

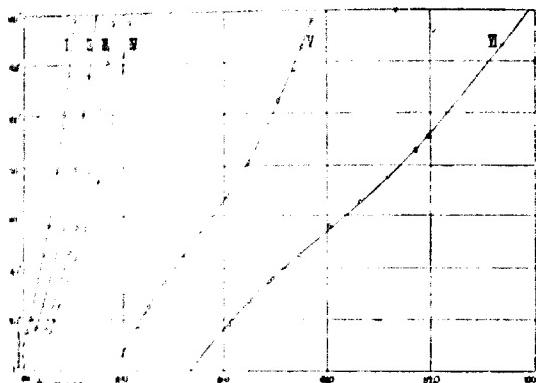
The first series of determinations having been made, the bath was emptied and removed, and the bulb *K* gradually immersed in liquid air, the outer tube of the gauge being at the same time exhausted by the water-pump to keep the pressure on both sides of the gauge nearly the same. The nitrogen trioxide condensed completely in the bulb *K*, no trace of any coloured gas being left in the bulbs I—VI. Bulb I was then sealed off and put aside for later determination of its volume. The liquid air was then removed and a further series of pressure-temperature measurements made with the correspondingly diminished volume of apparatus. Bulbs II, III, IV, V, VI, were then sealed off in turn, and the corresponding series of measurements made. After bulb IV had been sealed off a small superficial crack developed in the solid sealed-off end of bulb V. It was therefore thought advisable to seal off bulb V at once, lest the crack should spread and cause a leak. This was done, and it was found that no appreciable leak had occurred, since on putting *K* in liquid air a perfect vacuum was produced in the apparatus: moreover, bulb V, after remaining for several weeks, was found also to contain a perfect vacuum. The accident, however, made it possible to get six series of measurements only instead of seven. The volumes of bulbs I—VI were then determined by weighing them vacuous, and then opening under boiled-out water and weighing them full of water. The volumes at 25° were found to be:

Bulb I. 184.75 c.c. Bulb III. 92.17 c.c. Bulb V. 168.53 c.c.
Bulb II. 109.66 c.c. Bulb IV. 173.47 c.c. Bulb VI. 120.66 c.c.

The volume of the residue of the apparatus was found by opening it at *H* and sealing on a short length of tubing provided with a tap and connected with the Sprengel pump. The volumes of the added portion of tubing from *H* to the tap, and of the portion of

H cut off, were determined directly by the volume of water required to fill them. The nitrogen trioxide was pumped out repeatedly from the apparatus and replaced by air dried by passing through a long tube of phosphoric oxide. The apparatus was placed in a bath of water at a known temperature, the tap opened to equalise the pressure inside with that of the atmosphere, the barometer read and the tap closed. After exhausting the tubing between the tap and the pump, the tap was opened, the air pumped out from the apparatus, and collected and measured over mercury

FIG. 2.



in a calibrated vessel. This was done three times, the volumes obtained reduced to 25° being 201·79 c.c., 201·80 c.c., 202·00 c.c. (mean 201·86 c.c.), after allowing for the added and cut-off portions of the tubing.

The broken portions of the glass bulb which had contained the nitrogen trioxide were then collected and weighed, and the difference between this and the weight of the full bulb gave the weight of the nitrogen trioxide to be 0·3800 gram.

The results of the pressure temperature measurements at different volumes are given in Table I, and are plotted in Fig. 2.

TABLE I.

I (all bulbs on).		II (bulb I off).		III (bulb II off).	
T (corr.).	P.	T (corr.).	P.	T (corr.).	P.
14.85	106.2 mm.	16.6°	122.9 mm.	16.2°	141.8 mm.
25.2	115.8	25.6	134.2	25.6	153.5
35.1	125.7	36.0	147.8	36.2	168.0
45.15	136.3	45.4	159.2	46.2	184.1
56.6	145.7	55.8	171.4	56.1	196.3
77.8	159.5	78.95	192.6	78.15	218.2
96.05	170.8				
100.95	172.1	101.05	207.7	101.6	236.5
116.0	182.0	116.0	217.2	120.75	252.0
137.7	191.4	138.6	229.8	136.35	261.7

IV (bulb III off). V (bulbs IV and V off). VI (all bulbs off).

T (corr.).	P.	T (corr.).	P.	T (corr.).	P.
15.2°	148.3 mm.	17.3°	307.2 mm.	17.8°	470.8 mm.
20.3	155.1	22.6	318.2	27.0	506.9
25.2	161.5	24.9	326.4	34.8	542.2
35.3	177.6	34.7	355.8	35.8	547.4
43.8	192.1	45.1	388.9	44.95	594.9
55.3	209.7	54.45	418.4	56.1	646.1
74.2	233.0	67.65	467.7	65.4	699.8
95.3	258.1	81.5	504.2	75.4	748.6
117.1	275.1	96.8	542.8	85.85	795.4
136.5	290.8	104.92	556.2	90.9	818.3
		116.7	583.1		
		125.9	598.0		
		136.5	615.3		

The pressures at the temperatures 20°, 40°, 60°, 80°, 100°, 120°, 140° have been read off from the smoothed curves, the vapour densities at these temperatures, pressures and volumes (allowance being made for the expansion of the glass) calculated ($H = 1$), and the values given in Table II.

TABLE II.

20°.			40°.			60°.		
V. (litres). (H = 1).	P. (mm.). (H = 1).	Δ. (litres). (H = 1).	V. (litres). (mm.). (H = 1).	P. (mm.). (H = 1).	Δ. (litres). (H = 1).	V. (litres). (mm.). (H = 1).	P. (mm.). (H = 1).	Δ. (litres). (H = 1).
1.05116	111	29.55	1.05174	130	26.94	1.05234	147	25.33
0.80644	128	31.00	0.80690	153	27.77	0.80737	176	25.67
0.73659	146	31.21	0.75700	175	27.81	0.75740	200	25.87
0.66442	155	33.48	0.66478	187	29.63	0.66514	219	26.90
0.32250	311	33.52	0.32287	372	30.68	0.32284	439	27.65
0.20183	476	35.07	0.20194	570	32.00	0.20205	673	28.82

TABLE II. (*continued*).

80°.			100°.			120°.		
V. (litres).	P. (mm.).	Δ. (H=1).	V. (litres).	P. (mm.).	Δ. (H=1).	V. (litres).	P. (mm.).	Δ. (H=1).
1.05290	161	24.50	1.05348	172	24.16	1.05406	182	24.1
0.86784	194	24.67	0.86830	209	24.19	0.86877	220	24.1
0.75781	220	24.91	0.75822	238	24.32	0.75863	252	24.1
0.66550	241	25.90	0.66586	260	25.35	0.66622	278	24.1
0.32301	502	25.61	0.32318	551	24.65	0.32335	588	24.1
0.20216	768	26.75	0.20227	851	25.50	0.20238	924	24.1
140°.								
V. (litres).	P. (mm.).	Δ. (H=1).						
1.05456	192	24.00						
0.86924	232	24.09						
0.75904	265	24.10						
0.66658	284	24.80						
0.32352	620	24.23						
0.20249	988	24.29						

It is evident that the measurements made at the volume 665 c.c. (about) are affected by some constant error, since the values for the vapour density are in all cases obviously somewhat too large. These have therefore been neglected in the discussion which follows.

Discussion of Results.

It is seen from Table II. that the density of the gas varies from 35.07 at the lowest temperature and volume to 24.00 at the highest temperature and volume. These values are a good deal lower than those found by Baker, but the pressures at which the determinations are made are in practically all cases much lower than those used by him, and all his temperatures, with one exception, were atmospheric. Further there is much greater difficulty in completely drying an apparatus of the size and shape of that used in the present determinations than in drying the much simpler apparatus used by Baker.

For complete dissociation of N_4O_6 (or N_2O_5) into 2NO_2 and 2NO , which as Baker showed, occurs if the gas is in the slightest degree "wet," the vapour density would be 19: if it were all N_2O_5 it would be 38, and if all N_4O_6 76.

From Table II. it is seen that on increasing the temperature and volume the density decreases more and more slowly until it reaches the value 24.00, and it is evident that this value must represent very nearly the density of the completely dissociated gas. This assumption has been made in the calculations, and it is seen

that this density corresponds with something heavier than a simple mixture of NO_2 and NO molecules. The calculations are simplified by the fact that at 140° the dissociation of N_2O_4 into NO_2 is complete. For lower temperatures the values of the dissociation constant for the action $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, as found by Natanson and others have been used (Abegg, "Handbuch der Anorganischen Chemie," 3, III, 134). To explain the experimental results there are many possible assumptions. These may be represented by the following series of equations:

- (1) N_4O_6 (dry, not dissociating).
- N_4O_6 (wet) $\rightleftharpoons \text{N}_2\text{O}_4 + 2\text{NO}$.
- $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$.
- (2) N_2O_3 (dry, not dissociating).
- N_2O_3 (wet) $\rightleftharpoons \text{NO}_2 + \text{NO}$.
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$.
- (3) $\text{N}_4\text{O}_6 \rightleftharpoons 2\text{N}_2\text{O}_3$ (dry).
- $\text{NO} + \text{NO}_2$ (wet, not combining).
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$.
- (4) $\text{N}_4\text{O}_6 \rightleftharpoons \text{N}_2\text{O}_3 + \text{NO}_2 + \text{NO}$ (dry).
- $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$.
- (5) $\text{N}_4\text{O}_6 \rightleftharpoons 2\text{N}_2\text{O}_3$.
- $\text{N}_4\text{O}_6 \rightleftharpoons 2\text{NO}_2 + 2\text{NO}$ (the N_4O_6 dissociating in two ways).
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$.
- (6) $\text{N}_4\text{O}_6 \rightleftharpoons \text{N}_2\text{O}_3 + \text{NO}_2 + \text{NO}$.
- $\text{N}_4\text{O}_6 \rightleftharpoons 2\text{NO} + 2\text{NO}_2$ (the N_4O_6 dissociating in two ways).
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$.
- (7) N_4O_6 (dry, not dissociating).
- $\text{NO} + \text{NO}_2$ (wet, not combining).
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$.
- (8) N_2O_3 (dry, not dissociating).
- $\text{NO} + \text{NO}_2$ (wet, not combining).
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$.
- (9) $\text{N}_4\text{O}_6 \rightleftharpoons 2\text{N}_2\text{O}_3$ (dry, not further dissociating).
- $\text{N}_4\text{O}_6 \rightleftharpoons \text{N}_2\text{O}_3 + \text{NO}_2 + \text{NO}$ (dry, not further dissociating).
- N_4O_6 (wet) $\rightleftharpoons 2\text{NO}_2 + 2\text{NO}$.
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$.
- (10) $\text{N}_4\text{O}_6 \rightleftharpoons \text{N}_2\text{O}_3 + \text{NO}_2 + \text{NO}$ (dry, not further dissociating) (a)
- $\text{NO}_2 + \text{NO}$ (wet, not combining) (b)
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ (wet) (c)

All these assumptions were tested and were found to give results incompatible with the experimental data, with the exception of No. 10. Here it is assumed that the dry nitrogen trioxide in the liquid state is mainly in the form of N_4O_6 molecules, and that drying increases their amount. On vaporisation, these dissociate

to give N_2O_3 , NO_2 , and NO in equal volumes, the dissociation being very nearly complete at 140° , and on cooling the reverse change takes place. At the same time there are a certain number of molecules of NO_2 (or N_2O_4) and NO present, owing to incomplete drying, and these being "wet" do not react with each other to give nitrogen trioxide, nor take part in the action represented by equation (a) which is only concerned with dry molecules. The vapour density of a gas corresponding with complete dissociation according to equation (a) is 25.33: the observed density for complete dissociation is 24.00. From this can be readily calculated the amounts of "dry" N_2O_3 , NO_2 and NO , and of "wet" NO_2 and NO present. From the known dissociation constants for different temperatures for the action $N_2O_4 \rightleftharpoons 2NO_2$, the amounts of "wet" NO_2 and N_2O_4 present at any temperature and volume can be readily calculated. The vapour density at this temperature and volume for the whole mixture of gases being known by experiment, the density corresponding with (a) can be found, and hence the amounts of "dry" N_2O_3 , N_2O_4 , NO_2 and NO . The dissociation constant for the action $N_2O_6 \rightleftharpoons N_2O_3 + NO_2 + NO$ for the particular temperature t and volume V is then given by

$$K = \frac{C_{NO_2} V^2}{C_{N_2O_4} C_{NO_3} C_{NO}}.$$

The value of K was determined in this way for a series of volumes and temperatures, and the following results obtained:

TABLE III.

20°		40°		60°	
$V.$	$K.$	$V.$	$K.$	$V.$	$K.$
0.20183	118.0	0.20194	43.9	0.20205	13.6
0.32250	183.9	0.32267	67.2	0.32284	15.8
0.75559	164.7	0.75700	122.6	0.75740	40.9
0.86644	587.9	0.86690	157.8	0.86730	49.4
1.05116	187.7	1.05174	153.7	1.05234	50.6
80°		100°		120°	
$V.$	$K.$	$V.$	$K.$	$V.$	$K.$
0.20216	4.06	0.20227	2.18	0.20238	0.92
0.32301	6.07	0.32318	1.92	0.32335	0.92
0.75781	16.49	0.75822	6.01	0.75863	3.01
0.86784	13.23	0.86830	3.93	0.86877	2.89
1.05290	16.18	1.05348	4.90	1.05400	2.68
140°					
$V.$	$K.$				
0.20249	0.34				
0.32332	0.66				
0.75804	0.92				
0.86824	0.91				
1.05456	—				

The constancy here shown is evidently only very approximate except in the case of the three highest volumes, when it is quite fair, and, when the following points are noted, as good as can be expected. In the first place the value for the dissociation constant $K' = \frac{C_{NO_2} V}{C_{NO_3}^2}$, is, as Schreber has shown (*Zeitsch. physikal. Chem.*, 1897, **24**, 651), open to some doubt. In Natanson's results, indeed, K' in some cases varies as widely as K in the above table, and any error in the value of K' would be reflected in that obtained for K . Secondly, a very small error in the observed density will have a proportionately much greater error on the value of K : for example, an error of 0·4 per cent. in the observed density may produce a change of 25 per cent. in the value of K . Thirdly, the value of K is seen to be proportional to the square of the volume; and the experimental method used involved an error in the determination of the volume, namely, the unknown contraction in sealing off the bulb. In order to facilitate drying it was not considered advisable to use capillary tubes by which an appreciable error from this cause would have been avoided: with tubes of 3 mm. in diameter the error, though not great, may be appreciable: and it could be multiplied six times by the time the last bulb was sealed off. In accordance with this it is found that the values for K at the lowest volumes are less than those at the higher volumes. Fourthly, the boiling point of the liquid nitrogen trioxide being between 3° and 43° (Baker) it is quite possible that Boyle's Law is not obeyed by the vapour at the lower temperatures. If this is so the effect would be most marked at the lower volumes. There is, lastly, the possibility that, owing to the accident mentioned above, an infinitesimal amount of moist air may have leaked in through the crack before bulb V was sealed off, insufficient appreciably to affect the vacuum in the apparatus, but sufficient to cause complete dissociation of a portion of the trioxide to NO₂ and NO. Baker has shown that the amount of water vapour necessary to produce complete dissociation of a large amount of the trioxide is excessively small (T., 1907, **91**, 1864). This seems, on the whole, the most likely explanation of the low value of K as calculated at the two lower volumes, and it was therefore considered advisable to neglect the determinations at these volumes. On the other hand, the constancy of K at the three highest volumes may be considered as fairly satisfactory, and if the mean value of K for these volumes at different temperatures is taken and the vapour densities calculated, the agreement with the observed values is quite close, as is shown by the following table.

TABLE IV.

 $T = 20^\circ, K = 513.4.$

$V.$	Δ calc.	Δ obs.
1.05118	29.65	29.55
0.86644	30.77	31.09
0.75659	31.52	31.21

 $T = 40^\circ, K = 144.6.$

$V.$	Δ calc.	Δ obs.
1.05174	26.82	26.94
0.86690	27.56	27.77
0.75700	28.12	27.81

 $T = 60^\circ, K = 46.97.$

$V.$	Δ calc.	Δ obs.
1.05234	25.26	25.33
0.86737	26.68	26.67
0.75740	26.04	25.87

 $T = 80^\circ, K = 15.97.$

$V.$	Δ calc.	Δ obs.
1.05290	24.50	24.50
0.86781	24.68	24.67
0.75781	24.48	24.91

 $T = 100^\circ, K = 5.15.$

$V.$	Δ calc.	Δ obs.
1.05348	24.12	24.16
0.86830	24.23	24.19
0.75822	24.32	24.32

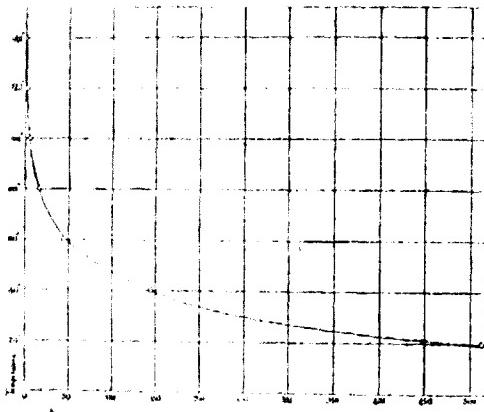
 $T = 120^\circ, K = 2.86.$

$V.$	Δ calc.	Δ obs.
1.05406	24.12	24.09
0.86817	24.14	24.14
0.75863	24.19	24.19

 $T = 140^\circ, K = 0.915.$

$V.$	Δ calc.	Δ obs.
1.05456	—	24.00
0.86924	24.08	24.09
0.75904	24.06	24.10

FIG. 3.



The relation between the value of K and the temperature is given by the curve shown in Fig. 3. At 0° , that is, somewhat below the boiling point, it is seen that the value for K is very high, indicating that the "dry" nitrogen trioxide under these conditions consists mainly of N_2O_6 molecules. At about 145° K becomes vanishingly small, and the dissociation into $N_2O_3 + NO_2 + NO$ may be taken to

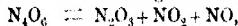
be practically complete. The value of the heat of the reaction,
 $N_4O_6 \rightleftharpoons N_2O_3 + NO_2 + NO$,
may be calculated by means of van't Hoff's equation,

$$\log_e \frac{K_2}{K_1} = \frac{Q}{2} \left(\frac{1}{T_1} - \frac{1}{T_2} \right),$$

and gives the following values:

T_1	T_2	Q = heat of formation of N_4O_6
20°	60°	11,308 cal.
60	100	14,185 ..
100	140	13,308 ..
Mean ...		12,933 cal.

It would appear, then, to be fairly well established that nitrogen trioxide at low temperatures consists mainly of N_4O_6 molecules, together with some N_2O_4 , NO_2 , and NO molecules, according to the extent of the drying. The vapour contains a mixture of N_4O_6 , N_2O_4 , NO_2 , and NO molecules reacting according to the equation



mixed with some "wet" N_2O_4 , NO_2 , and NO molecules.

The extent to which the dissociation of the N_4O_6 proceeds under different conditions of temperature and pressure, and the amounts of the "wet" gases present, are illustrated by the following figures, which give the calculated composition of the gas under different conditions.

TABLE V.

	20°		60°	
Volume ...	0.20183	1.05116	0.20205	1.05234
N_4O_6	0.18732	0.11240	0.10050	0.03150
N_2O_4	0.00468	0.10214	0.10809	0.14255
NO_2 "dry" ...	0.03915	0.06182	0.06543	0.08028
NO	0.02553	0.04032	0.04266	0.05627
NO_2 "wet" ...	0.03516	0.03755	0.03810	0.03832
N_2O_4	0.00317	0.00077	0.00022	0.00000
NO	0.02499	0.02499	0.02499	0.02499
100° .				
Volume ...	0.20277	1.05348	0.20249	1.05456
N_4O_6	0.03544	0.00402	0.00720	0.00000
N_2O_4	0.14062	0.15634	0.15474	0.15835
NO_2 "dry" ...	0.08511	0.09463	0.09366	0.09584
NO	0.05551	0.06171	0.06108	0.06251
NO_2 "wet" ...	0.03832	0.03832	0.03832	0.03832
N_2O_4	0.00000	0.00000	0.00000	0.00000
NO	0.02499	0.02499	0.02499	0.02499

The effect of prolonged drying of the liquid appears to be to enable the NO_2 and NO molecules to combine to give N_4O_6 , which

in the dry state dissociates to give N_2O_3 , NO_2 , and NO in equal volumes, the N_2O_3 not further dissociating.

It further seems likely that the N_4O_6 molecules in the liquid state are blue, and in the gaseous state both N_4O_4 and N_2O_3 are colourless, or nearly so. This is supported by the following observation. A specimen of the trioxide prepared by Professor Baker, and dried for four years, shows an almost pure blue colour at the ordinary temperature, and it may be taken that there are very few "wet" NO_2 or N_2O_4 molecules remaining under these conditions. On gentle warming, however, the blue liquid changes to green, the colour becoming blue again on cooling. This is probably due to the yellow NO_2 molecules produced by the dissociation $N_4O_6 \rightleftharpoons N_2O_3 + NO_2 + NO$ giving with the blue N_4O_6 molecules a green mixture. Ordinary "wet" liquid nitrogen trioxide is green, owing to the mixture of blue N_4O_6 with a relatively large amount of "wet" NO_2 . The blue specimen of very dry nitrogen trioxide still gives a brownish-red vapour, owing to the formation of NO_2 in the dissociation of the gaseous N_4O_6 . At very low temperatures all specimens of nitrogen trioxide, very dry or slightly wet, become quite blue. This would be due to the fact that at these temperatures any "wet" NO_2 molecules would completely associate to give colourless N_2O_4 molecules, which would then no longer produce a green colour with the blue N_4O_6 .

The thanks of the author are due to Professor Baker for the specimen of nitrogen trioxide and for much valuable advice, and to Mr. H. F. V. Little for assistance in the calculations.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S.W.

CXV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XX. Isomeric Solvents.*

By THOMAS STEWART PATTERSON and ERNEST FERGUSON POLLOCK.

In previous parts of this investigation it has been shown to what a remarkable extent the rotation of active compounds, but particularly that of ethyl tartrate, may be varied by subjecting these substances to the influence of different neutral solvents, and in a number of cases the results due to isomerism in the solvent have

been considered. Thus the effect of ortho-, meta-, and para-substitution is often very great, as, for instance, in the nitro-derivatives of benzene and toluene (T., 1908, 93, 1836), in the nitrophenols (T., 1910, 97, 2110), or the three toluidines (T., 1912, 101, 241). It has also been shown that quite a marked difference in regard to solvent effect exists between the *syn*- and the *anti*-forms of various oximes, and upon this fact has been based a method for determining the rate of transformation of these isomerides, both in the homogeneous condition (T., 1907, 91, 504; *ibid.*, 1907, 40, 2564; T., 1908, 93, 1041; *Proc. Roy. Soc. Glasgow*, 1911, 42, 10, 26) and also in solution in various liquids, as well as one for determining the influence of various neutral solvents on the velocity of this reaction (T., 1912, 101, 26, 2100). Similarly, it has been shown that the change from the α -form to the β -form of ethyl formylphenylacetate (T., 1907, 91, 519), and of ω -isonitrotoluene into ω -nitrotoluene (T., 1908, 93, 1048), and of ammonium cyanate into carbamide (*ibid.*, p. 1050), could be followed in the same way.

It is thus clear that comparatively subtle forms of isomerism may often be readily detected or indicated by the different solvent action of the two varieties, and it seems not improbable that a method such as this might on occasion prove useful in settling a doubtful constitution. Thus, for example, as will be shown presently, since the esters of thiocyanic acid appear to produce in ethyl tartrate a higher rotation than do the corresponding esters of *iso*-thiocyanic acid, the solvent influence of two isomeric esters belonging to these classes might be sufficient to discriminate between them.

We have therefore thought it desirable to investigate a little further this question of the relationship between solvent influence and isomerism, with the results given below.

The active compound used at first was *isobutyl* malate, which, wherever possible, was made up to a concentration of about $c=10$ with the isomeric solvents. The solution was then examined as regards its rotation at a few temperatures in the neighbourhood of 20° , and by interpolation the observed rotation at 20° was obtained. The density was determined directly at 20° , and the specific rotation calculated. The results are given in the following table.

*Influence of Solvents on the Rotation of isoButyl Malate.*isoButyl Malate, α_D^{∞} (100 mm.) = -10.69° , $[\alpha]_D^{\infty} = -10.26^\circ$.

Solvent	<i>p.</i>	α_D^{∞} (100 mm.)	<i>d.</i>	$[\alpha]_D^{\infty}$
Methyl thiocyanate	9.451	-1.19°	1.0695	-11.75
Ethyl thiocyanate	10.213	-1.20	1.0117	-11.61
Ethyl isothiocyanate	10.085	-1.24	1.0012	-12.28
isoButyl thiocyanate	10.6407	-1.06	0.9837	-10.34
isoButyl isothiocyanate	10.657	-1.06	0.9832	-10.43
Ethyl ethylacetacetate	10.212	-1.19	0.9833	-11.84
Nitrobenzene	8.516	-1.11	1.1855	-10.99
Tetrabromoethane	3.5961	-0.23	2.7736	+2.30

From these numbers it will be noticed that the rotation in ethyl thiocyanate is lower—that is, more negative—than in ethyl thiocyanate, and that the same holds true, but to a very much less extent, for the isoButyl esters of these two acids. The value for the rotation in methyl thiocyanate is given in the table, but the corresponding value for the isothiocyanate could not be obtained at the same concentration, since the solvent crystallises out. It was intended to compare the rotations of isoButyl malate in ethyl *B*-ethoxycrotonate with that in ethyl ethylacetacetate, but the former solvent also crystallises out at the concentration and temperature of the experiments.

It appears, however, from these results that the rotation of isoButyl malate is, comparatively speaking, not very sensitive to solvent influence, and in order to ascertain what variation of rotation with change of solvent might be expected as a maximum, we examined this ester in nitrobenzene on the one hand, and in *s*-tetrabromoethane (acetylene tetrabromide) on the other. It will be seen from the table that whilst nitrobenzene has but little effect on the rotation of the ester, *s*-tetrabromoethane raises its value to $+2.30^\circ$. Although this is a considerable change, it is only about one-third of that which is caused in the rotation of ethyl tartrate by the same change of solvent, namely, from $+31.55^\circ$ in nitrobenzene (*p.* 10) (T., 1908, **93**, 7852) to -10° in *s*-tetrabromoethane (T., 1908, **93**, 371). On account of this greater sensitivity of ethyl tartrate, we decided to use it in our subsequent experiments, the results of which are given in the following table:

*Influence of Solvents on the Rotation of Ethyl Tartrate.*Ethyl Tartrate, $\alpha_D^{\infty} + 9.142^\circ$, $[\alpha]_D^{\infty} + 7.58^\circ$.

Solvent	<i>p.</i>	α_D^{∞} (100 mm.)	<i>d.</i>	$[\alpha]_D^{\infty}$
Methyl thiocyanate	60.625	+6.873°	1.1148	+9.87
Methyl isothiocyanate	61.396	+5.585	1.1449	7.95
Ethyl thiocyanate	9.981	+1.198	1.0255	11.71
Ethyl isothiocyanate	10.166	+0.048	1.0147	0.37

Influence of Solvents on the Rotation of Ethyl Tartrate
(continued).

Ethyl tartrate, $\alpha_D^{20} + 9.142^\circ$, $[\alpha]_D^{20} + 7.58^\circ$.

Solvent	<i>p.</i>	α_D^{20} (100 mm.).	<i>d.</i>	$[\alpha]_D^{20}$.
<i>iso</i> -Butyl thiocyanate	10.588	+0.628	0.9749	6.23
<i>iso</i> -Butyl <i>isothiocyanate</i>	10.670	-0.102	0.9662	-0.99
<i>n</i> -Butyl alcohol	12.035	+0.935	0.8445	+9.18
<i>iso</i> -Butyl alcohol*	9.996	-0.475	0.8307	5.72
<i>sec</i> -Butyl alcohol	11.88	+0.57	0.8404	5.71
<i>tert</i> -Butyl alcohol	12.127	+0.35	0.8263	3.49
Ethyl ethylacetacetate	62.934	+4.695	1.1115	6.72
Ethyl <i>S</i> -ethoxycrotonate	62.958	+3.405	1.1113	4.86
Ethyl <i>C</i> -acetylacetacetate	9.02	+1.001	1.1020	10.01
Ethyl <i>O</i> -acetylacetacetate	9.375	+1.411	1.0759	13.99
Acetone	10.01	+1.003	0.8226	12.18
"	25.055	+2.600	0.8727	11.89
Diethyl ketone	11.791	+1.055	0.8497	10.53
Methyl propyl ketone	11.883	+1.093	0.8442	10.90
Diethyl sulphite	9.381	+0.514	1.0933	7.84
Ethyl ethylsulphonate	8.659	+0.430	1.1631	4.27
Diethyl carbonate	10.109	+0.650	0.9949	6.46
Ethyl orthocarbonate	10.803	+0.403	0.9432	3.95
<i>n</i> -Cresol	9.612	+3.387	1.0598	33.24
<i>m</i> -Cresol	9.635	+4.305	1.0496	42.57
<i>p</i> -Cresol	9.592	+4.721	1.0500	46.87
Methyl acetoacetate	10.21	+1.256	1.0882	11.30
" "	25.227	+2.049	1.1070	10.56
" "	50.461	+5.402	1.1388	9.40
Ethyl acetoacetate	10.471	+0.972	1.0450	8.88
" "	25.0834	+2.158	1.0689	8.05
Ethyl methylacetacetate	50.1892	+4.335	1.1117	7.71
Ethyl dimethylacetacetate	10.2349	+0.884	1.0156	8.51
" "	10.2808	+0.923	1.0275	8.82
" "	25.167	2.121	1.0536	8.00
" "	50.312	3.781	1.1002	6.83
Acetaldehyde	49.086	+8.45	1.0125	17.02
Paracetalddehyde	49.99	+2.154	1.0974	3.93
Allyl alcohol	28.27	+3.143	0.9305	11.95
" Propyl alcohol*	49.81	5.335	1.0010	10.70
" " "	25	1.470	0.8790	6.73
<i>n</i> -Cresol methyl ether	10.06	+0.880	0.9981	8.77
<i>m</i> -Cresol methyl ether	10.166	+0.495	0.9063	4.89
<i>p</i> -Cresol methyl ether	10.042	+0.70	0.9921	7.03

* T., 1901, 79, 478.

† T., 1901, 79, 209.

The changes here are decidedly more marked. Ethyl thiocyanate as a solvent raises the rotation of ethyl tartrate to some slight extent—by about 4° —whereas ethyl *isothiocyanate* depresses it by a little more than 7° , so that the difference in solvent influence of these two substances is quite considerable—more than 11° . The *isobutyl* esters of these two acids produce analogous effects, but the difference is not quite so great as in the former case. The difference quoted in the table between the rotations of solutions of ethyl tartrate in methyl thiocyanate and methyl *iso*-

thiocyanate is still less, being just about 2° , but it must be noticed that the concentration at which these values were determined is much higher (in dilute solution the methyl thiocyanate separated out of the solution), and doubtless if values could have been obtained at lower concentrations the specific rotations would show a considerable difference, comparable with that found for the ethyl and isobutyl esters.

An interesting case of different solvent action is presented by the four butyl alcohols. *N*-Butyl alcohol raises slightly the rotation of the dissolved ethyl tartrate; *is*-butyl alcohol depresses it by an almost equal amount; *sec*-butyl alcohol has practically the same effect as *is*-butyl alcohol, whilst *tert*-butyl alcohol reduces it still further. The considerable differences exhibited here seem to justify the idea that this method might in certain circumstances be used to discriminate between the various classes of alcohols.

Since a considerable amount of attention has been devoted to the investigation of the influence of multiple bonds on the rotation of active compounds containing them, it seemed of interest also to ascertain whether any general effect is to be observed in the solvent action of unsaturated liquids. In an earlier paper (T., 1907, 91, 1838) it has been shown that ethyl fumarate and ethyl maleate exercise a considerably greater solvent influence on the rotation of ethyl tartrate than does ethyl succinate, and, further, that ethyl fumarate has almost the same effect as ethyl maleate. We have therefore examined two pairs of isomerides of a somewhat similar type, namely, ethyl ethylacetacetate and ethyl β -ethoxycrotonate on the one hand, and ethyl *C*-acetylacetacetate and ethyl *O*-acetylacetacetate on the other. Of the former pair, it will be observed that the unsaturated compound depresses the rotation of the ethyl tartrate to a greater extent than does ethyl ethylacetacetate, whereas of the latter pair, the unsaturated compound, the *O*-acetyl derivative, raises the rotation of the ethyl tartrate to a greater extent than does the isomeric liquid. It ought, however, to be noticed that the concentration for the former pair of solvents is much greater than for the latter.

In this connexion, we have also examined allyl alcohol as a solvent for ethyl tartrate, and find that it produces a decided rise of the rotation, whereas the corresponding saturated alcohol brings about a slight diminution.

Of the ketones examined, acetone produces the highest rotation, whilst the unsymmetrical compound, methyl propyl ketone, has a somewhat greater solvent influence than has the symmetrical diethyl ketone, but in the case of diethyl sulphite and ethyl ethylsulphonate the symmetrical compound has comparatively little

influence, whilst the unsymmetrical derivative depresses the rotation of the ethyl tartrate to a not inconsiderable extent.

Although diethyl carbonate and ethyl orthocarbonate are not isomeric, it seemed of interest to compare their effects also, and it will be seen that whilst diethyl carbonate has a slight depressing influence, ethyl orthocarbonate has a similar but greater effect.

Of the three cresols, the *p*-derivative has the most marked influence, but is followed somewhat closely by the *m*-isomeride, and at a longer interval by *o*-cresol. The behaviour of other disubstituted benzenes in this respect has been summarised in a previous paper (T., 1912, 101, 244). The various cresol ethers have, as in other somewhat similar cases (T., 1910, 97, 2118), very much smaller influences than the corresponding cresols; the change in solvent influence in passing from a cresol to the derived ether is not the same in all cases, however, but is greatest in the *p*-derivatives and least in the *o*-derivative.

An interesting comparison is that between acetaldehyde and paracetaldehyde, the former raising the rotation of the dissolved ester very considerably, whilst the latter has the opposite effect.

Methyl acetoacetate raises the rotation of ethyl tartrate more than does ethyl acetoacetate, whilst there is but little difference between the influences of ethyl acetoacetate and its methyl and dimethyl derivatives.

Some of the solutions dealt with here were examined over a greater range of temperature than the others, and as the data may be of value in connexion with the effect of temperature on rotation, they are given in the table below. They show no characteristics sufficiently striking to call for special remark.

Solvent: Acetone.

The acetone was Kahlbaum's No. II. It was treated with dehydrated potassium carbonate, and distilled through a Hempel tube. The middle fraction, b. p. 56·3°, was used.

p=10·01.

<i>t</i>	13°	17°	36·7°	40°
<i>d</i>	0·8302	0·8280	0·8043	0·7944
α_b^l (249·6 mm.)	2·42	2·448°	2·682	2·763
$[\alpha]_b^l$	11·87	11·86°	13·35	13·92

p=25·055.

<i>t</i>	11·6°	16·2°	25·5°	32°	36°
<i>d</i>	0·8820	0·8769	0·8665	0·8593	0·8550
α_b^l (249·6 mm.)	6·21°	6·388	6·682	6·855	6·968
$[\alpha]_b^l$	11·25°	11·61	12·33	12·76	13·03

Solvent: Methyl acetoacetate (D_4^{m} 1.0757). $p = 10.2123$.

	15.3°	22°	35.1°	43.2°	54°
<i>t</i>	1.092	1.086	1.072	1.064	1.052
<i>d</i>					
<i>a'</i> (170 mm.)	2.07	2.18	2.26	2.34	2.40
[<i>a</i>] _{<i>o</i>}	10.92	11.57	12.15	12.67	13.15

 $p = 10.2268$.

	16.9°	23.5°	35.1°	44.2°	57.3°
<i>t</i>	1.1103	1.1030	1.0910	1.0810	1.0670
<i>d</i>					
<i>a'</i> (170 mm.)	4.93°	5.13°	5.46°	5.65°	5.87°

 $[a]_o$

	10.35°	10.84°	11.67°	12.18°	12.82°
<i>t</i>					
<i>d</i>					
<i>a'</i> (70 mm.)					

 $[a]_o$

	9.04	9.51°	10.86°	11.59°	12.1°
<i>t</i>					
<i>d</i>					

 $[a]_o$ Solvent: Ethyl acetoacetate (b. p. 75°/12 mm.; D_4^{m} 1.0284). $p = 10.4715$.

	14	18	46°	51°	57.5°	63°	71.5°
<i>t</i>							
<i>d</i>	1.0510	1.0470	1.0185	1.0132	1.0065	1.0010	0.9925
<i>a'</i> (400 mm.)	3.53	3.80	4.92	4.95	5.23	5.30	5.46

	8.92	8.66	11.48	11.66	12.40	12.64	13.13
<i>t</i>							
<i>d</i>							

 $[a]_o$

	14	20.4°	30°	40.5°	50.5°
<i>t</i>					
<i>d</i>	1.075	1.068	1.058	1.048	1.038
<i>a'</i> (170 mm.)	3.42°	3.69°	4.09°	4.47°	4.77°

 $[a]_o$

	7.46°	8.10°	9.06°	10.01°	10.78°
<i>t</i>					
<i>d</i>					
<i>a'</i> (70 mm.)					

 $[a]_o$

	15.2°	20.4°	30.7°	43.1°	54.2°
<i>t</i>					
<i>d</i>	1.117	1.111	1.101	1.088	1.077
<i>a'</i> (70 mm.)	2.78	3.03	3.42	3.84	4.13

 $[a]_o$

	7.09	7.76	8.84	10.05	10.92
<i>t</i>					
<i>d</i>					

Solvent: Ethyl methylacetoacetate (D_4^{m} 0.9974). $p = 10.349$.

	13°	23°	30°	41°
<i>t</i>				
<i>d</i>	1.0225	1.0126	1.0055	0.9943
<i>a'</i> (400 mm.)	3.25°	3.66°	3.90°	4.28°

	7.77°	8.81°	9.48°	10.51°
<i>t</i>				
<i>d</i>				

Solvent: Ethyl dimethylacetoacetate (D_4^{m} 1.0101). $p = 10.2808$.

	11.9°	21.8°	35.8°
<i>t</i>			
<i>d</i>	1.035	1.025	1.0115
<i>a'</i> (170 mm.)	1.48°	1.59°	1.78°

	8.18°	8.87°	10.08°
<i>t</i>			
<i>d</i>			

$p = 25.1675.$

<i>t</i>	13.2°	21.9°	38.4°	48.8°	57.1°
<i>d</i>	1.0602	1.0518	1.035	1.024	1.016
α'_b (70 mm.)	1.33°	1.52°	1.78°	1.91°	2.01°
$[\alpha]_b^l$	7.14°	8.23°	9.78°	10.61°	11.26°

 $p = 50.3124.$

<i>t</i>	12.6°	20.1°	32.2°	40.8°	51.0°
<i>d</i>	1.107	1.100	1.088	1.079	1.069
α'_b (70 mm.)	2.55°	2.86°	3.33°	3.60°	3.94°
$[\alpha]_b^l$	6.54°	7.38°	8.69°	9.47°	10.46°

Solvent: Paracetaldehyde.

 $p = 49.99.$

<i>t</i>	20°	33.1°	42.9°	57°	67.5°
<i>d</i>	1.0975	1.092	1.070	1.053	1.041
α'_b (70 mm.)	1.508°	2.344°	2.77°	3.354°	3.63°
$[\alpha]_b^l$	3.93°	6.19°	7.40°	9.05°	9.95°

Solvent: Allyl alcohol.

 $p = 28.27.$

<i>t</i>	8.6°	23.2°	35.3°	46.2°	55.0°
<i>d</i>	0.941	0.9275	0.9165	0.9063	0.8975
α'_b (100 mm.)	2.97°	3.18°	3.40°	3.51°	3.61°
$[\alpha]_b^l$	11.17°	12.13°	13.16°	13.70°	14.23°

 $p = 49.81.$

<i>t</i>	11.5°	21.3°	34.2°	43.6°	53.0°
<i>d</i>	1.009	1.000	0.988	0.9795	0.971
α'_b (100 mm.)	5.04°	5.38°	5.84°	6.11°	6.35°
$[\alpha]_b^l$	10.03°	10.80°	11.86°	12.52°	13.13°

In conclusion, we have to acknowledge our indebtedness to Mr. D. P. McDonald, who made a number of the observations recorded here, and to the Council of the Chemical Society for a grant from the Research Fund which defrayed most of the cost of this investigation.

ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW.

CCXVI.—Studies in Catalysis. Part I. Hydrolysis of Methyl Acetate, with a Theory of Homogeneous Catalysis.

By ALFRED LAMBLE and WILLIAM CUDMORE McCULLAGH LEWIS.

It is well known that temperature has a marked influence on reaction velocity, the general value of the temperature-coefficient being 2.5 for a rise in temperature of 10° when the reaction is proceeding at room temperature. This increase of velocity with temperature cannot, of course, be explained from the mere increase in kinetic movement, for this should only mean an increase of 2 per cent. in the velocity of the reaction for the same change of temperature. It is clear that the temperature effect must be due to some influence on, or connected with, the internal structure of the molecules taking part in the reaction. Now, the phenomenon of catalysis in homogeneous solution has made us familiar with the acceleration of reactions at constant temperature, and this, therefore, must be due to some internal effect on, or connected with, the structure of the molecules. It seems, therefore, not unreasonable to expect that the two effects are intimately connected, and possibly identical in nature. This was the initial assumption in this work. Now, as was first suggested by Arrhenius (*Zeitsch. physikal. Chem.*, 1889, **4**, 226), the effect of temperature has been ascribed to the existence of an equilibrium between so-called "active" and "inactive" molecules, such equilibrium being sensitive to temperature change; and hence an increase in temperature, by bringing into existence more "active" molecules, causes a reaction velocity very much in excess of what one would expect on a merely kinetic view. Arrhenius has even deduced an expression, $\frac{d \log k}{dT} = \frac{A}{T^2}$, showing the effect of temperature in terms of a quantity A , which on this view is taken to be half the energy change involved in the transformation of 1 mol. of "inactive" to "active." If such "active" and "inactive" molecules exist, it appears reasonable to expect that a catalyst, such as hydrogen or hydroxyl ions, simply acts in shifting this equilibrium. (It is not necessary to go into any possible mechanism of such a process, such as intermediate compound or complex ion-formation.) If the above conclusion, that the catalyst shifts over the equilibrium, is true, it can be tested at once by determinations of the reaction-velocities at different temperatures with different amounts of catalyst. For, evidently, if the addition

of the catalyst shifts this equilibrium between the "active" and "inactive" form, it is conceivable that sufficient catalyst could be added to change a relatively large amount of "inactive" to "active" molecules. It would follow, then, on determining the temperature-coefficient, that when the catalyst is present in large quantities, such a temperature-coefficient should be smaller than that observed when the reaction is not catalysed, or only feebly so. For, when much catalyst is present, the transformation from "inactive" to "active" would have already taken place (on the above assumption regarding the identity in nature of the temperature-effect and the catalytic effect), and therefore temperature should have less additional accelerating effect.

In spite of the fact that numerous catalytic reactions have been investigated, an examination of the literature has shown that in no case have catalyst and temperature been simultaneously varied. The experiments detailed in the following section were therefore carried out for the purpose indicated above.

EXPERIMENTAL.

The reaction studied was the hydrolysis of methyl acetate by hydrochloric acid of various concentrations. Five c.c. of the ester were added to 100 c.c. of the acid, and the reaction proceeded in flasks fitted with air-tight stoppers. The temperature was maintained at $25 \pm 0^{\circ}5$. From time to time, 2 c.c. of the reaction mixture were withdrawn, and run into about 50 c.c. of conductivity water to stop the reaction, the time of withdrawal from the flask being noted to the nearest second by means of a stop-watch. The solution withdrawn was then titrated with $N/20$ -baryta. The velocity-constants were calculated to the base "*e*" from the formula $k = \frac{2.30}{t} \log \frac{a}{a-x}$. Two experiments were performed in each case, and the mean value of *k* obtained from the two. In the following table, *t* is the time from the start in minutes, *x* is the number of c.c. of baryta required to neutralise the amount of reaction-mixture withdrawn, and *k* is the velocity-constant, calculated to the base "*e*."

TABLE I

Hydrolysis of Methyl Acetate with 0·1005N-Hydrochloric Acid at 25°.

(Bracketed values of k omitted from calculation of mean value of k .)

<i>t.</i>	<i>a.</i>	$k \cdot 10^3$	<i>b.</i>		
			<i>t.</i>	<i>a.</i>	$k \times 10^3$
0	10·18	—	0	10·33	—
11·5	10·54	[0·600]	10·5	10·68	[0·613]
23·22	11·00	0·653	23·75	11·05	[0·571]
43·49	11·65	0·641	43·20	11·85	0·660
83·50	13·10	0·658	83·61	13·20	0·637
99·91	13·59	0·660	99·61	13·80	0·665
127·83	14·39	0·644	127·70	14·60	0·641
145·15	15·05	0·681	144·3	15·22	0·655
169·20	15·48	0·652	160·0	15·80	0·644
196·33	16·55	0·649	196·6	16·75	0·641
	63·38	0·654	∞	64·54	0·652

Mean value of k for both experiments = $0\cdot653 \times 10^{-3}$.

The above table will serve as an illustration of the general character of the figures obtained in these experiments. The following table contains the mean values of two experiments, and their mean, obtained by the hydrolysis of methyl acetate with various strengths of hydrochloric acid at 25°.

TABLE II.

Hydrochloric acid.	$k \times 10^3$.		
	(1).	(2).	Mean.
0·5024N	3·521	3·500	3·510
0·8275N	5·967	6·036	6·001
1·80N	15·92	16·26	16·09
2·429N	19·73	21·81	20·78

It will be observed that the above experiments have been carried into a region of catalyst concentration much greater than that usually employed. It was hoped that this relatively high concentration of catalyst would shift over, to a measurable extent, the equilibrium between the "active" and "inactive" molecules of methyl acetate if such exist. Before proceeding to determine the corresponding reaction-velocities at 35°, it was necessary to obtain data by which the same hydrogen-ion concentration could be maintained at 35° as existed at 25°. It has been suggested by Goldschmidt (*Zeitsch. physikal. Chem.*, 1910, **70**, 627; 1912, **81**, 30), Snetlilage (*Zeitsch. Elektrochem.*, 1912, **18**, 539; *Zeitsch. physikal. Chem.*, 1913, **85**, 211), and Acree (*Amer. Chem. J.*, 1912, **48**, 352) that, in addition to the hydrogen ion, the undissociated

molecule of the acid has a catalytic effect, but so long as the same hydrogen-ion concentration persists at 35° as at 25° in the corresponding experiment, the concentration of the catalyst remains the same, whether the catalyst be the hydrogen ions, the undissociated acid molecule, or both. Accordingly, a series of conductivity measurements for the acid used was performed, together with the necessary viscosity measurements, the details of which are given below. A special conductivity cell of high resistance was used, as the concentration of the acid was so great that the conductivity was very high. The cell consisted of a horizontal glass tube about 30 cm. long and 2 sq. cm. in cross-section, and the electrodes were sealed in at the ends. The cell was filled and emptied by means of two side-tubes, and was found to give very satisfactory readings. The results are given in the following tables.

TABLE III.
Conductivity of Hydrochloric Acid in Aqueous Solution.

Acid normality.	Specific conductivity at		Equiv. conductivity at	
	25°.	35°.	25°.	35°.
0.5024	0.1804	0.2051	359.7	409.1
0.8275	0.2827	0.3196	341.6	386.2
1.280	0.4045	0.4543	316.0	355.0
1.800	0.5225	0.5909	290.2	328.3
2.429	0.6322	0.7101	260.2	292.5

The viscosities of the solutions of hydrochloric acid used were determined relative to water at 25° by means of a Scarpa viscometer (*Gazzetta*, 1910, **40**, ii, 261). The values obtained are given below in table IV.

TABLE IV.
Relative Viscosities (to Water at 25°) of Aqueous Hydrochloric Acid Solutions.

Acid normality.	Relative viscosity at	
	25°.	35°.
0.5024	1.06	1.052
0.8275	1.059	1.087
1.280	1.062	1.082
1.800	1.152	1.115
2.429	1.154	1.107

Previous investigation has shown that the mobility of the ions can be corrected for viscosity by simply multiplying by the inverse ratio of the viscosity relative to that of water, when the viscosity is in no case very different from that of water. The corrected conductivities obtained in this way are given in table V.

TABLE V.
*Conductivity of Hydrogen Chloride in Aqueous Solution, Corrected
 for the Viscosity of the Solution.*

Acid normality.	Specific conductivity at		Equiv. conductivity at	
	25°.	35°.	25°.	35°.
0.5024	0.1912	0.2158	380.6	429.5
0.8275	0.2993	0.3474	361.6	419.8
1.280	0.4295	0.4916	335.6	384.0
1.800	0.6010	0.6589	335.5	366.0
2.429	0.7297	0.7801	300.3	323.7

The values of the equivalent conductivity at infinite dilution were calculated from the formula $\epsilon_1 = \epsilon_{15}(1 + k(t - 18) + k'(t - 18)^2)$ (Kohlrausch and Holborn, "Leitwerte der Elektrolyte," p. 199). Hence Λ_∞ at 25° is 424.6, and Λ_∞ at 35° is 490.3.

From this α , the degree of dissociation, was calculated, and the values obtained are given in table VI.

TABLE VI.
*Degree of Dissociation, α , and Hydrogen-ion Concentration, $[H^+]$,
 in Equivalents per Litre at 25° and 35°, of Hydrogen Chloride
 in Aqueous Solution.*

Acid normality.	α at 25°.	α at 35°.	$[H^+]$ at 25°.	$[H^+]$ at 35°.
0.5024	0.8964	0.8760	0.4503	0.4400
0.8275	0.8515	0.8561	0.7047	0.7086
1.280	0.7903	0.7830	1.0120	1.002
1.800	0.7900	0.7464	1.4220	1.344
2.429	0.7071	0.6601	1.7180	1.603

The values of the hydrogen-ion concentration obtained in table VI were plotted against the normality of acid at the two temperatures 25° and 35°. From the graph it was then determined what concentrations of acid at 35° gave the same hydrogen-ion concentrations as those already employed at 25°. The results obtained are shown in table VII. It will be seen that up to the concentration 1.28% the values of the acid normality are practically coincident, and only diverge beyond this concentration.

TABLE VII.
Acids of Equivalent Hydrogen-ion Concentration at 25° and 35°.

Acid normality, at 25°.	Acid normality, at 35°.	Hydrogen-ion concentration.
0.5024	0.5024	0.4503N
0.8275	0.8275	0.7047
1.280	1.300	1.0120
1.800	1.935	1.422
2.429	2.920	1.718

In the case of 0·1005*N*-hydrochloric acid, it can be assumed that, like *N*/2- and *N*-hydrochloric acid, the degree of dissociation is practically the same at 25° and 35°.

The velocity-constants with the acid strengths given in column 2 were then determined at 35°, and the results obtained are given below.

TABLE VIII.

Hydrochloric acid.	$k \times 10^4$.		
	(1).	(2).	Mean
0·1005 <i>N</i>	1·649	1·677	1·663
0·5024	8·781	8·892	8·836
0·8275	15·38	15·15	15·26
1·935	37·60	38·08	37·84
2·429	64·12	62·83	63·47

In table IX is given a list of temperature coefficients, these coefficients being the ratio of the velocity-constant at 35° to the corresponding constant at 25°.

TABLE IX.

Table of Temperature-coefficients.

Acid normality.	Mean value of	Mean value of	k_{35}/k_{25}
	k_{25}	k_{35}	
0·1005	$0·653 \times 10^{-4}$	$1·663 \times 10^{-4}$	2·547
0·5024	$3·510 \times 10^{-4}$	$8·836 \times 10^{-4}$	2·520
0·8275	$6·001 \times 10^{-4}$	$15·26 \times 10^{-4}$	2·542
1·800	$16·09 \times 10^{-4}$	$37·84 \times 10^{-4}$	2·353
2·429	$20·78 \times 10^{-4}$	$63·47 \times 10^{-4}$	3·054

Discussion of Results.

The result of these experiments, in which the catalyst has been varied over a very considerable range of concentration, shows conclusively that there is no tendency at all for the temperature-coefficient of a strongly catalysed reaction to be less than that of a weakly catalysed reaction. This is sufficiently contrary to what would have been expected on the conception of "active" and "inactive" molecules that one is justified in seeking for some other explanation that will apply equally to temperature effect and to the effect of the catalyst. This conclusion regarding the non-existence of active and inactive molecules (in the Arrhenius sense) is supported, to a certain extent, by the work of Taylor (Idd. K. *Vetenskapsakad. Nobelinst.*, 1913, **2**, No. 34), who points out that the influence of neutral salts on the hydrolysis of esters is independent of the ester being hydrolysed. Owing to the generality and comparability of catalysis in homogeneous solutions, as, for example, the approximate proportionality between the velocity of the reaction and the concentration of the catalyst

on the one hand, and the generality of the temperature-coefficient which is of the same order for a whole series of widely varying reactions, on the other hand, one is tempted to seek for some physical basis which would apply equally to both. In the first place, Marcellin recently (*Compt. rend.*, 1914, **158**, 161) has deduced on a thermodynamic basis, with the addition of some considerations based upon the theory of probability, an equation identical in form with that found empirically by Arrhenius for the effect of temperature on the velocity-constant. Marcellin, however, treats the effect of temperature as a purely physical one dependent on the increase in internal energy of the reacting molecule. He deduces the equation $\frac{d \log k}{dt} = \frac{E}{RT^2}$, where E is defined as the "critical" energy, that is, the energy absorbed by the molecule, in excess of the average energy possessed by all molecules, before it becomes reactive. We suggest as more suitable that Marcellin's "critical energy" be defined as *critical increment*, since E denotes the extra amount of energy which has to be added above the average value (u). The term "critical energy" could then be used to denote the total amount of energy which the molecule must possess in order to make it react. A convenient symbol for this quantity would be E_c , that is, $E_c = E + u$. Marcellin's investigation shows that the temperature-effect can be accounted for on a purely physical basis; in other words, it does not require the assumption of "active" and "inactive" chemical isomericides. Since, therefore, on Marcellin's view, there are no "inactive" and "active" molecules, in the chemical sense, in mass action equilibrium, one would not expect the presence of a catalyst to diminish the temperature-coefficient, which is thus in agreement with the experimental results outlined above.

Having seen how the effect of temperature can be accounted for on a purely physical basis, it is natural to apply this to the effect of the catalyst. This is all the more necessary, because of the many conflicting views that have been put forward from time to time in endeavouring to obtain a purely "chemical" explanation for catalysis. Accordingly, it is suggested that catalysis is essentially a "radiation" phenomenon, and this is the more likely in view of the recent chemical significance of radiation, as expressed, in general, in the quantum theory, and more particularly for the present purpose in Einstein's photochemical law (*Inn. Physik*, 1912, [iv], **37**, 832) and in the work of Krug (*Zeitsch. Elektrochem.*, 1911, **17**, 453). According to Einstein, a photochemical reaction (that is, one due to radiant energy), takes place by the absorption of quanta, one molecule being decomposed

by one quantum ($=hv$, where h = Planck's constant and v = the vibration frequency of the energy being absorbed or emitted), a law which is approximately supported by experiment. Thus Bodenstein (*Zeitsch. physikal. Chem.*, 1913, **85**, 339) has shown that the limits, in general, are from one to four quanta. Now Trautz (*Zeitsch. wiss. Photochem.*, 1906, **4**, 160) has pointed out that even "ordinary" or thermal reactions may be regarded as ultimately photochemical, with the distinction, of course, that such "ordinary" reactions are due to infra-red radiation. Kruger (*loc. cit.*) has also shown how chemical phenomena, such as the processes of solution, solubility, solution pressure, and electrolytic dissociation, may be explained on the basis of radiation, these being linked up, in turn, with the dielectric constant of the solvent.

Returning now to Marcellin's expression, $\frac{d \log k}{dt} = \frac{E}{RT^2}$, it is clear that the presence or absence of a catalyst should not affect the value of E , and, in agreement with this, we have found that the temperature-coefficient of a reaction is independent of the quantity of catalyst present. In the case of the hydrolysis of methyl acetate (as for various other reactions), the temperature-coefficient for a rise of 10° about room temperature is 2.5. Therefore, since

$$\frac{d \log k}{dt} = \frac{E}{RT^2}$$

it follows that

$$\log \frac{k_{308}}{k_{298}} = \frac{E}{R} \left(\frac{1}{298} - \frac{1}{308} \right).$$

whence E is equal to 16,800 calories per gram-mol.

Now, since there are 6.85×10^{23} molecules per gram-mol., the actual mean energy added to a single molecule, that is, the critical increment per molecule, to give it the critical energy, E_c , is $16,800 \times 4.2 \times 10^{-7}$, that is, 1.03×10^{-12} ergs. Now can this energy be obtained from infra-red radiation? Let us assume, for simplicity, that methyl acetate absorbs monochromatic infra-red radiation, and that the increase in energy is effected by means of one or more quanta of such radiation. If v is the frequency, c the velocity of light, and λ the wave-length of the light, then, since λ for methyl acetate may be taken to have a mean value 5μ (see Coblenz, *Pub. Carnegie Inst. Wash.*, 1905, **35**), on applying Einstein's theory, strictly, that one quantum ($=hv$) is necessary to make a molecule "photochemically" react, hv should be

$$\frac{5 \times 10^{-7} \times 3 \times 10^{10}}{7.5 \times 10^{-4}}, \text{ that is, } 0.262 \times 10^{-12} \text{ ergs. It will be seen,}$$

therefore, that the critical increment, E , per molecule is of the order of four quanta of the size mentioned.

We may also calculate inversely what frequency, v , will be necessary in order that one quantum may have the same value as E . In other words, equating $\hbar v$ to 1.03×10^{-12} ergs, it is found that $v = 1.57 \times 10^{11}$. This corresponds with a wave-length of 1.9×10^{-4} cm. ($\approx 1.9 \mu$). Since this lies in the region of absorption of methyl acetate, absorbable infra-red radiation will therefore be sufficient to account fully for the magnitude, E . Hence it follows that, so far as the temperature-coefficient of reaction-velocity is concerned, the mechanism whereby the increase in internal energy is attained can be accounted for by radiation.

Now, assuming that catalysis is likewise due to the absorption of radiation, one must note, in the first place, that radiation can only be emitted by a charged particle vibrating. The simplest view regarding the mechanism is to consider it as due to the hydrogen ion as a whole, leaving out for the present the question of disturbances of the electronic orbits inside the ion itself. It is suggested that the ion is vibrating between neighbouring molecules (mainly solvent molecules), and that the radiation-emission is due to such vibrations, analogous to its production by vibration of charged atoms in a solid, such as a metal. The reasons for regarding the type of motion of a dissolved ion as being vibrational, rather than translational, are as follows. Nernst and Lindemann (*Zeitsch. Elektrochem.*, 1911, **17**, 817) have shown that the phenomenon of fusion of a solid can be regarded as due to the vibrating atoms of the solid having just attained an amplitude comparable with the distance apart of the atoms. The fusion or liquid may therefore at the melting point be still considered as possessing vibrating atoms (molecules or ions), and since moderate changes in temperature have relatively little effect on the molecular spacing of liquids, it seems a justifiable extension of Lindemann's view to apply it to a liquid, at least over a temperature range not too far removed from the melting point. The second argument in favour of this is the extremely small diffusion coefficient possessed by a substance dissolved in a liquid, compared with the diffusion of a gas at the same temperature, although, of course, the kinetic energy (not necessarily of translation, but possibly of vibration, neglecting rotation) is the same for the two. The dissolved ions must be in rapid movement, but they pass and repass over a centre of gravity, the position of which only changes very slowly with time, and an enormous number of to and fro movements occurs in a second. To-and-fro movement over a fixed or relatively fixed, point or plane constitutes vibration, the ampli-

tude of vibration in the case considered being the mean distance between two molecules of the solvent. The ion is repelled on colliding* at each end of its swing. This supplies the potential energy (which must be present, as well as kinetic in a true vibration), which is usually ascribed to an attraction exerted on the vibrating body from its centre of gravity. In other words, attraction exerted by the point of rest can be exactly reproduced by equal and opposite repulsions from limiting positions of swing. The molecules of the solvent are, of course, undergoing the same type of motion. If the actual motion of the hydrogen ion is of the type described, it will be capable of absorbing and emitting radiation. It must be remembered that, on emitting radiation (in a "bundle" of one or more quanta), the ion momentarily loses its energy, but immediately proceeds to absorb energy from the surrounding reservoir, so that at any particular interval of time all the hydrogen ions will not possess the same energy. Their energy can be represented by a mean value—some ions will possess more than this quantity, some less.

We shall now proceed to calculate the order of magnitude of the radiation emitted. The gram-molecular volume of water at 0° is 18 c.c. practically. The domain allotted to a single molecule is therefore $\frac{18}{7 \times 10^{23}} = 2.6 \times 10^{-23}$ c.c. in round numbers. Hence

the radius of each domain is 1.84×10^{-8} cm., and the centres of two adjacent water molecules are separated, on the average, by a distance 3.68×10^{-8} cm. The limiting volume (that is, the volume at absolute zero) for one gram-molecule of water is approximately 17 c.c. Hence the actual radius of a single molecule is approximately 1.8×10^{-8} cm. Thus the actual radius of a molecule is of the same order of magnitude as the distance apart of two adjacent molecules. For water—and indeed for most liquids at the ordinary temperature—the range of swing or free path is thus an exceedingly small quantity, namely, of the order 10^{-8} to 10^{-9} cm. The same order naturally holds for the distance of a completed swing. Now the mean velocity of a hydrogen ion at 25° in temperature-equilibrium is easily obtained, knowing its kinetic energy at this temperature. This mean velocity (more accurately the root mean square velocity) is 2.73×10^5 cm. per second, in round numbers. Hence the time required for a complete swing of a hydrogen ion over a distance comparable with the distance apart of the solvent molecules lies between the limits 10^{-8} and 10^{-9} , that is,

* Nothing is really known of the ultimate nature of a collision. Possibly it is electromagnetic repulsion.

3.7×10^{-16} to 3.7×10^{-15} seconds. This is the periodic time and the reciprocal is the frequency v , or the number of vibrations per second. The frequency, therefore, lies between 2.7×10^{15} and 2.7×10^{16} . This is the frequency of the radiation emitted, if any be emitted at all. The wave-lengths corresponding with these values are 11μ to 1.1μ , that is, wave-lengths in the "moderate" infra-red region, this region being at the same time that over which methyl acetate has marked absorption. The infra-red absorption of methyl acetate, so far as the measurements of Coblenz (*loc. cit.*) have gone, extends from 1.6μ to 14μ . The maximum absorption occurs between the limits 5.8μ and 11μ , this absorption being extremely marked. It will be seen, therefore, that the radiation emitted by the vibration of a hydrogen ion corresponds in wave-length with the radiation for which methyl acetate has marked absorption. If we take the mean value of the frequency of vibration of a hydrogen ion to be 1.48×10^{15} , the energy of one quantum

$$hv = 6.55 \times 10^{-2} \times 1.48 \times 10^{15} = 0.97 \times 10^{-12} \text{ ergs},$$

a quantity obviously of the same order as the extra amount of energy required to be added to "decompose" one molecule of methyl acetate, namely, 1.03×10^{-12} ergs, according to the calculation from Marcelin's expression. It follows, therefore, that the energy emitted by the vibration of a hydrogen ion is sufficient to supply the "critical increment," that is, the energy which a methyl acetate molecule must absorb, according to Marcelin, before it becomes reactive. Of course, it must be pointed out that the considerations regarding the source of the radiation from the ion as due simply to its vibration to and fro between two neighbouring molecules have been put forward as being the simplest possible conception of the process. The actual mechanism may be more complex.

The Energy of Vibration of other Ions.

On the basis of the mechanism suggested, more slowly moving ions will give rise to frequencies of smaller value, and therefore, in the case of heavier ions, the velocity, and consequently the vibration frequency, decreases. The frequencies, and the energy of the quanta corresponding with these frequencies, have been calculated for the commoner ions in aqueous solution, both when these are regarded as anhydrous and as hydrated (using the values computed by Riesenfeldt and Reinhold (*Zeitsch. physikal. Chem.*, 1909, **66**, 672). It is unnecessary to give these in detail, as the relative positions occupied are altered in the two cases. All the quanta are less than those corresponding with the hydrogen ion.

No catalytic effects were observed with potassium and lithium chlorides in the hydrolysis of methyl acetate.

General Considerations.

As regards the question of the possible activity of the undissociated molecule, experiments are now in progress, as well as with other consequences of the radiation mechanism suggested, such as the effect of a solute on the dissociation of the solvent, the catalytic effects of fluorescing substances, the abnormal dissociation of strong electrolytes, neutral salt action, the anti-catalytic effect of water in alcoholic solutions, and anti-catalysts or "preservatives" in general.

It should be pointed out once more that the main idea put forward in the present communication lies in the application of infra-red radiation as the physical basis of the effects observed without any insistence upon a particular mechanism whereby the radiation is caused. That suggested is the simplest conceivable, but it may yet be necessary to regard the question from the point of view of the internal structure of the hydrogen ion, such, for example, as the continuous change from a dehydrated to a hydrated state, this being a dynamical view intermediate between the two opposing statical "chemical" views, one of which ascribes the catalytic effect to the hydrated ion, the other to the unhydrated ion. In order to obtain emission from a charged particle, it appears necessary, in view of Bohr's theory (*Phil. Mag.*, 1913, **vii**, 25, 10), to conceive of passage from one position of stability to another, the "positions" of stability being respectively the hydrated and unhydrated states. In any event, it appears likely that the distances involved will be molecular, that is, of the order 10^{-8} cm., and hence infra-red radiation of the same order as that already calculated would be emitted.

When a reaction proceeds without a catalyst (in the ordinary sense), it may be assumed that the normal radiation density existing in the medium is itself sufficient to give to the molecules the requisite "critical energy." The idea, therefore, of ascribing catalytic effects as due to localised increase in radiation density is a logical extension of this view.

Summary.

- (1) Experiments have been carried out which show that the temperature-coefficient of a reaction is independent of the concentration of the catalyst. This is contrary to what one would expect

on the assumption of "active" and "inactive" chemical isomers.

(2) On the basis of Marcelin's physical explanation of the effect of temperature on reaction-velocity, a radiation theory has been suggested to explain the phenomenon of catalysis in homogeneous solution. Certain other consequences which follow from this have been pointed out.

THE MUSEUM LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
THE UNIVERSITY OF LIVERPOOL.

CXVII. *The Metallography of German Silver.*

By FRANK CHARLES THOMPSON.

From the physicochemical point of view, the system copper-zinc-nickel, to which the German silvers belong, has received detailed examination from Tafel ("Metallurgie," 1908, Vol. V., p. 413). Almost the whole of the more directly industrially important knowledge of these alloys, however, is contained in a paper by Hudson (*J. Inst. Metals*, 1913, i, 109), who, starting with the cast metal, traced its structural alterations on rolling and annealing. Only one composition of metal, however, was examined, and alterations in structure with alloys of different qualities were not considered. Since these alloys, however, consist entirely of Tafel's α -solution, they are metallographically strictly comparable with the α -brasses, and in addition to the researches mentioned above, information of the greatest value may be obtained from the accounts of work done on the latter alloys. In particular may be instanced the classical paper of Charpy ("Contributions à l'étude des alliages," Paris, 1901, p. 1), which dealt both mechanically and micrographically with their working and annealing.

Our present knowledge of the micrography of the German silvers may be briefly summarised as follows.

The commercial alloys consist entirely of the α -solid solution, since the appearance of the β -phase is accompanied by a brittleness that renders them incapable of receiving the work to which they must be subjected. In the cast state, the structure consists of cored crystals, which in these nickeliferous alloys are remarkably persistent under both mechanical and thermal treatment. Annealing at a proper temperature will in time remove this coring, giving place to a structure consisting entirely of allotrimorphic crystals, in which, however, unless the annealing has been very prolonged, traces of the cast structure may still be recognised.

Like all α -solutions, these alloys are rolled cold, which treatment produces, if carried far, an indefinite linearity in the direction of greatest extension. The cored structure often still persists after repeated rolling and annealing. When the cold-worked metal is annealed above a certain minimum temperature, a recrystallisation is effected, the degree of coarseness of which is increased as the annealing temperature is raised and as the time is prolonged.

The present research has been carried out, for the most part, on actual commercial specimens subjected to ordinary works treatment, and the results are typical of the industrial alloys.

With a few exceptions, which will be mentioned, the sections have been etched with 5 per cent. ferric chloride solution, in which only so much hydrochloric acid is present as is furnished by the hydrolysis of the salt.

EXPERIMENTAL.

(a) Oxygen in German Silver.

The difficulty of determining accurately the oxygen in brasses and German silver is well known, and ordinary micrographs of the alloys do not show non-metallic impurities. By heating together cupric oxide and zinc, Turner (*J. Inst. Metals*, 1912, ii, 2) has observed a reaction, accompanied by a considerable evolution of heat, in which the oxygen is transferred from the copper to the zinc, and hence has drawn the conclusion that in the copper-zinc alloys the oxide present is that of zinc. Exactly how this occurs is not quite so clear, but Turner is of the opinion that it is probably in a kind of fine suspension "mechanically entangled." The author hopes to be able to show that this is exactly the form in which the oxygen is, in all probability, present in the alloys under consideration.

A direct solution to the problem would appear to be impossible, but the application of the principle of "maximum work" should indirectly afford an answer. According to this theory, a system is in its stable condition when those components are present which have been formed with the evolution of the maximum amount of heat. Thus assuming the oxygen in German silver to be present as an oxide, it follows from the theory that it will be that oxide the heat of formation of which is the greatest.

The following list of the heats of formation of the lower oxides of copper, zinc, and nickel is taken from the tables of Landolt and Bornstein:

Oxide.	Heat of formation.
Cu ₂ O	42.3 (mean of two).
NiO	59.7
ZnO	85.0

These results, then, indicate very strongly that, as Turner concluded for the copper-zinc alloys, from an entirely different consideration, the oxide present in German silver is that of zinc.

In order to determine the exact mode of occurrence of the zinc oxide, a series of specimens of good commercial German silver of varying percentages of nickel was examined at a high magnification after polishing, but without etching. In all cases, very fine black inclusions were visible, of one of the most marked of which Fig. 1 is a photograph, taken at 1000 diameters. The structure would faintly suggest a radiating or globular eutectic, but for the present "mechanically entangled" would seem the best descriptive

(b) *The Influence of Deoxidants.**

In the metallography of alloys, such as the α -solutions, which consist entirely of a single phase, the size of the allotrimorphic crystals must in all cases be a point of the greatest importance. With a view to determine the influence of deoxidants, a series of four alloys was examined. The essential composition of each was the same, but whilst two had received no addition, 0·25 per cent. of manganese had been added to one fusion and 0·5 per cent. of aluminium to the other. The alloys after casting were rolled into sheets and annealed.

On examination at a magnification of 60 diameters, the two untreated alloys were composed of crystals the mean area of which was 0·3 sq. cm., and thus readily observed. At the same magnification the crystals of the deoxidised alloys were so small as to be individually invisible, and a mere matt-surface effect was observed. At higher magnifications the mean area was found to be 0·0007 sq. cm.

In the aluminium alloy, an incomplete network faintly to be seen may afford an explanation of the idea held by certain makers of German silver that the presence of even small amounts of aluminium is detrimental to the properties of the metal.

This remarkable refining action of the small additions of manganese and aluminium is the more curious, as, at any rate in the case of manganese, the whole amount added had passed into the slag, hardly a trace remaining in the alloy.

The finer structures of the deoxidised alloys imparted to them a higher tensile strength than that of the untreated metal, and in view of the fact stated above, that no chemical difference existed between the treated and untreated specimens, no explanation

* A deoxidant is an element added (usually a metal) to the molten alloy before the latter is cast to eliminate oxygen which has been dissolved during the melting.

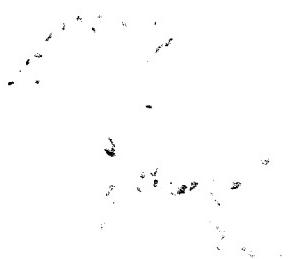


Fig. 1

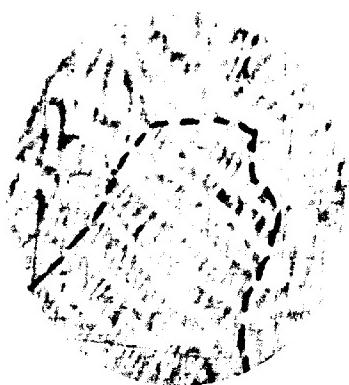


Fig. 2 — 50^x



Fig. 2 — 50^x

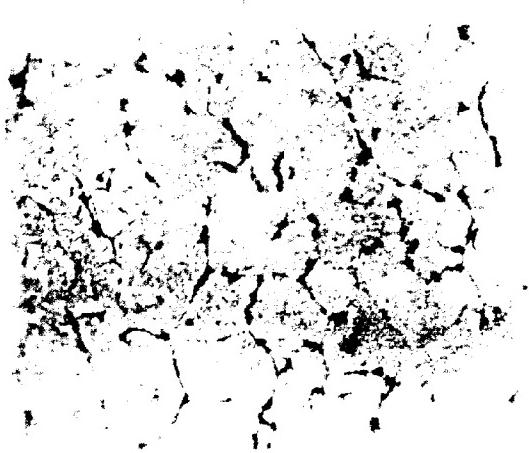
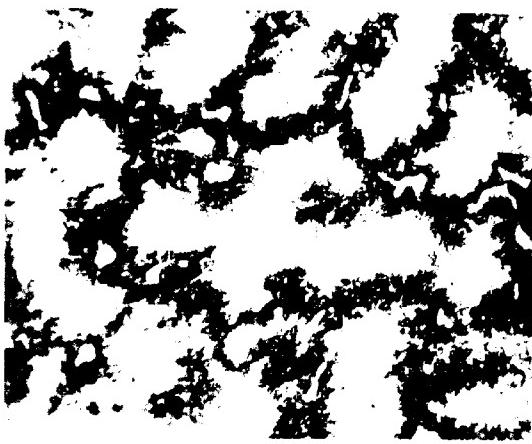


Fig. 1. - *lithology*.





appears to meet the case so well as that of the amorphous cement theory of the intercrystalline boundaries developed by Rosenhain (Rosenhain and Ewen, *J. Inst. Metals*, 1912, ii, 149; 1913, ii, 119) and his co-workers. Several other observations, all pointing in the same direction, have been made during the preparation of this paper. Thus, Humfrey (*J. Iron and Steel Inst. Carnegie*, Vol. 16, 1913) has recently shown that in stressed ferrite the slip bands show a tendency when approaching the crystalline boundaries to bend round and to approach at a smaller angle, indicating that these junctions do possess properties differing considerably from those of the interior of the crystal. A similar conclusion may be arrived at from the curvature of the twinned crystals in German silver which has been cold worked. After the distortion, the twinned portions show a marked tendency to retain their original angles with the boundaries of the crystals. At a small distance from the boundaries, however, which is still great compared with the actual thickness of these, the limits of the twins become curved, following the direction of elongation of the crystals.

The same alloys were of interest in another direction. Trouble sometimes occurs in the working of German silver due to "riffling," this effect is a corrugation of the surface of the article during drawing, etc. Tensile test-pieces were prepared and broken from each of the alloys, when two showed the appearance markedly, and the others, which had been deoxidised, were free. The untreated alloys were, in comparison, coarsely crystalline, while the crystals of the treated ones were exceedingly minute, and it is in this crystal size that the source of the trouble seems to lie. "Riffling" is apparently due to certain crystals being squeezed out at the surface under pressure from adjacent ones. If the crystals are large the surface will lose its smoothness, but if minute the effect will be inappreciable.

The addition of a suitable deoxidant would thus reduce the liability to this defect, and, in addition, the author has reason to believe that the adherence of the deposit during electroplating is also improved at the same time.

The grain-refining influence of such additions is not restricted to the alloys under consideration, but appears to be a fairly general phenomenon. The reduction in the crystal size of a Muntz metal by the addition of 2 per cent. of manganese, although not so marked as for German silver, is distinctly noticeable.

(c) *The Effect of Pronounced Overheating.*

Fig. 2 is the photograph of a German silver of high nickel content which, as a result of drastic over-annealing, had become almost

entirely devoid of ductility. Despite repeated cold rolling and annealing, a very definite "casting" structure is evident, which would appear to owe its reintroduction to the overheating. The grain size of this alloy, as shown in Fig. 4 at 300 diameters, cannot be the cause of the brittleness.

In order to decide whether such heat treatment is capable of reproducing the cast pattern, the burnt specimen was annealed for four hours at 759°. The structure after this treatment was that of a perfectly normal alloy, and all traces of the dendritic markings had totally disappeared.

The same specimen was next reheated for one hour to just below the solidus, about 1000°, when a structure very closely resembling that of Fig. 2 was again obtained, although the branching was scarcely so well shown.

Exactly what is the mechanism of these changes is hardly apparent. The casting pattern was, on the average, perhaps 2.5 mm. long, whilst the diameter of the crystals shown in Fig. 4 was of the order of 0.042 mm., so that the two would seem to have nothing in common. When a similar German silver in the cast state is burnt (Fig. 3), a markedly different structure is obtained and vastly larger crystals. The most probable explanation seems to be that the casting pattern is a remnant of the structure of the original ingot, but so faintly preserved that, in ordinary circumstances, it is not seen. The tendency of the zinc to volatilise at the high temperature, especially from those parts where the core structure remains, may conceivably give a sponginess which, after etching, would show this faint structure.

This curious reproduction of the "as cast" pattern by over-annealing is exactly comparable with the well-known reintroduction of the martensitic pattern in overheated steel forgings. If the overheating be sufficiently drastic, the structure becomes so intensely angular as to be indistinguishable from that of an untreated casting.

It has recently been shown by C. Chappell (*J. Iron Steel Inst.*, 1914, 1) that the recrystallisation of cold worked ferrite is effected by the deformed crystals splitting up into many smaller secondary ones, and a similar method of recrystallisation seems to hold for German silver if the dendritic markings of Fig. 2 are the remains of the original crystalline structure. The area outlined in this photograph would then represent part of one primary crystal, which Fig. 4 indicates must have broken up into some hundreds of smaller ones when recrystallisation occurred during annealing after cold work.

Fig. 4 is of the same section as Fig. 2 after the annealing and

reburning, but taken at a magnification of 300 diameters. The first point of interest is that, although it represents a rolled and annealed German silver, practically no trace of twinning remains, and the section confirms the conclusion of Edwards and Carpenter (*J. Iron Steel Inst.*, 1914, i), that by prolonged heating all traces of twinning may be eliminated from a forged and annealed metal much below the melting point. This comparative absence of twins in overheated German silver may afford valuable evidence, additional to the crystal size, to the works investigator when dealing with material suspected of over-annealing. A second point of interest in connexion with Fig. 4 is the peculiarly broad crystal junction, probably due to the volatilisation of zinc in their vicinity, and further evidence of the validity of the amorphous cement hypothesis. Since a material in the amorphous condition has a higher vapour tension than in the crystalline, other things being equal, where such material exists there should also burning occur.

(d) *Influence on the Structure of Different Compositions.*

When the average grain size of a 70/30 brass is compared with that of a German silver, the finer crystallisation of the latter at once suggests that the presence in the solution of nickel has a decided tendency to reduce the coarseness of the grain. To determine how far this is true for varying qualities of German silver, a series of seven alloys was examined, ranging in nickel percentage from 7 to 22 per cent., which had received ordinary commercial treatment. Fig. 5 is a photograph at 100 diameters of the 12 per cent. alloy, and the following list will indicate how very marked is the diminution in the size of the crystals as the percentage of nickel in the alloy increases.

Nickel. Per cent.	Mean area of crystal. Sq. cm.
12	0.015
15	0.0025
22	0.0005

The chemical composition of the alloys is here the main factor, but since the annealing temperature of the lower nickel alloys is, in general, somewhat higher than that for the more highly nickeliferous ones, this may also have exaggerated slightly the effect of the nickel. This refining action has a counterpart in the metallography of steel, where the action in reducing the grain size of 3 per cent. of nickel is most marked.

The effect of the copper-zinc ratio on the structure has not been examined in detail, since the copper percentage in the alloys is

almost fixed. In the one case with 15 per cent. of nickel which was examined, an increase in the percentage of copper of 4 per cent. yielded a small refining action, which, however, might well have been due to slight alterations of the conditions of annealing.

Throughout the range of nickel percentage examined, no alteration in the type of twinning could be detected. In all cases there was, for the most part, of the repeated type, with also some size-twinning, and throughout the series corrosion pits suggested eutectic crystallisation, although no accurate measurement was made. With the exception of the size of the crystals, the only other effect on the structure of the increase in the nickel percentage is the greater persistence of the cored crystals during rolling and annealing.

(e) Lead and Tin.

Lead is practically totally insoluble in brasses and German silver. In the cast state, the lead separates out as globules, which on rolling become elongated to threads in the direction of the greatest extension. These threads, however, are not continuous, but break up into a series of globules roughly spherical in shape. Fig. 6 is a photograph of a forging of German silver with about 13 per cent. of lead. The specimen has been polished only, and not etched.

Fig. 7 is of an alloy with about 2·5 per cent. of tin in the cast state. A new slate-grey constituent has appeared, strongly resembling the similar grey constituent in bronzes beyond the limit of the solution. The constituent may well be of similar composition, either Cu₃Sn or a solution rich in it. It shows, however, no trace of the eutectoid structure of the constituent of the bronze. The well-known brittleness of intermetallic compounds affords a ready explanation of the inferior mechanical properties of German silver rich in tin. The structure of this alloy hardly appears to the author to suggest the eutectic stated by Law ("Alloys," p. 175) to be formed by the addition of tin to German silver.

Analogy between German Silver and Steel.

Several times during this paper analogies have been pointed out between the metallography of German silver and steel, and these may be extended. It may well be that for certain purposes the use of one alloy for the other may be possible, whilst inferences drawn from the metallography of one metal may further the study of the other.

The most obvious points of similarity are:

- (1) In practice, the annealing temperature-range from 900° to

100° is the same for each, and the temperature falls as the percentage of nickel increases in the non-ferrous alloys, and as the carbon increases in the steel.

(3) In each case, overheating will cause a reintroduction of the cast structure, with an accompanying loss of ductility.

(3) The mechanical properties of German silver are not dissimilar from those of a normal mild steel.

(4) In each case, increased nickel content means a diminution in the size of the grain.

(5) The mechanism of the recrystallisation after cold work appears to follow the same course for both metals.

(6) As shown by the austenitic steels, the original cast structure of each is the same, and there is reason to believe that the peculiar persistence of the cored structure in the German silver has a counterpart in the ferrous metals.

Summary.

(1) The oxygen in German silvers is probably present as finely disseminated oxide of zinc.

(2) Deoxidants have a marked influence in giving a finer crystal line structure, accompanied by better mechanical properties.

(3) A curious reproduction of the "as cast" structure has been found in burnt metal.

(4) Lead and tin both cause the separation of distinct components, probably lead and a compound of copper and tin respectively.

(5) Marked analogies exist between the metallography of German silver and steel, and between their mechanical and annealing properties.

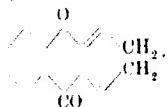
The best thanks of the author are due to Dr. H. C. Greenwood, of Messrs. William Hutton and Sons, Sheffield, for several of the specimens, and to Mr. J. H. Wreaks, Lecturer in Metallography in the University of Sheffield, for much help and advice.

METALLURGICAL DEPARTMENT,
UNIVERSITY OF SHEFFIELD.

CCXVIII.—*The Colouring Matters of Rhamnus catharticus.*

By JOSEF OESCH and ARTHUR GEORGE PERKIN.

According to the work of Tschirch and Polacco (*Arch. Pharm.*, 1900, **238**, 459), the yellow, tinctorial constituents yielded by berries of *Rhamnus catharticus* (Hungarian berries) are quite distinct from those given by the berries of the various species of *Rhamnus* which constitute the Persian berry proper, and now well known to consist of rhamnetin, rhamnazin, and quercetin. Thus according to these authors, in addition to rhamnoemodin and certain other allied non-tinctorial compounds, with which the present paper is not concerned, there could be isolated from the berries of *R. catharticus* four hitherto unknown yellow, crystalline substances, to which the names rhamnocitrin, β -rhamnocitrin, rhamnochrysin, and rhamnolutin were assigned. Although the constitution of these compounds was not ascertained, it appears likely that rhamnocitrin, $C_{13}H_{10}O_5$, was the trihydroxy-derivative of the dihydioxanthone,



and rhamnolutin a new tetrahydroxylavone isomeric with luteolin and fisetin. Again, rhamnochrysin $C_{13}H_{10}O_7$, was probably an oxidation product of rhamnocitrin, whereas the latter and β -rhamnocitrin, $C_{13}H_{10}O_5$, closely resembled the β -rhamnetin which Schutzenberger describes as obtainable from Persian berries. β -Rhamnocitrin is quite distinct from rhamnetin, $C_{12}H_{10}O_5$, and indeed, in all these compounds methoxy-groups were absent.

It is somewhat remarkable that Tschirch and Polacco were unaware that the true formula of rhamnetin is $C_{16}H_{12}O_7$ (*Herzog Monatsh.*, 1888, **9**, 548; 1891, **12**, 172), and that the so-called β -rhamnetin is with little doubt quercetin (T., 1895, **67**, 502).

Valiaschko and Krasowski (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1502), and Krasowski * (*ibid.*, 1510), on the other hand, strongly criticise this work of Tschirch and Polacco, and contend that from the botanical relationship existing between the Persian berries and those of *R. catharticus*, and the similarity of their dyeing properties, it is only to be anticipated that the same colour-

* For a translation of this paper, which is written in the Russian language, we are indebted to the kindness of Mr. T. H. Pope.

ng matters will be yielded by both. As a matter of fact, the compounds of Tschirch and Polacco could not be isolated, although the presence of rhamnetin and quercetin was easily detected. Rhamnolutin is possibly rhamnetin, as the melting point of the acetyl derivative, 183—184°, would appear to suggest, whereas rhamnocitrin is exactly like quercetin and rhamnetin in its reactions. Again, instead of rhamnochrysin, a mixture of quercetin and emodin was obtained. Further, xanthorhamnin, the glucoside of rhamnetin, is present in these berries.

At the outset of this work we were unaware of Krasowski's paper, our object being chiefly the study of the rhamnocitrin of Tschirch and Polacco, for although flavone derivatives are extremely common throughout nature, the closely allied xanthone group of which this compound was apparently a member appears to be but poorly represented. Having, however, soon satisfied ourselves as to the nature and properties of this compound, a study of the other colouring matters which can be obtained from the berries has been carried out, with the results given in this paper. As it seemed possible that the divergent results of these former workers might have been occasioned in the one case or the other by the accidental use of berries not derived from *R. catharticus*, special pains have been taken to ensure the botanical authenticity of the material here employed.

EXPERIMENTAL.

Four kilos. of the berries were extracted with eight litres of boiling water for three hours, the mixture was filtered, and the residue washed with 1·5 litres of hot water. Experiments were first carried out on the substances removed from this extract by agitation with ether, but this eventually proved to be unnecessary, and fortunately so, for not only did the mixture separate from the ether with difficulty, but very little colouring matter was removed thereby. The small quantity of the products isolated in this manner, however, closely resembled in property those described by Tschirch and Polacco.

It was found better at once to hydrolyse the glucosides present in the aqueous solution, and for this purpose sulphuric acid to the extent of 1·5 per cent. was added, and the mixture boiled for two hours. A granular precipitate gradually separated, which increased in quantity on cooling, and this was collected and washed, and, when dry, consisted of 352 grams of a dark brown powder. In order to remove a trace of plant wax which was present, it was extracted with a little boiling benzene, only a minute amount of yellow colouring matter being removed thereby.

The product in the finely powdered condition was now thoroughly extracted with boiling ether, and the extract evaporated, whereby a yellow, crystalline residue (*A*), weighing 102 grams, remained. The residue insoluble in ether, which possessed a dark brownish-black tint, was practically free from colouring matter, and was possibly largely a phlobaphen produced from a phobatannin by the action of the boiling acid. The crystalline residue (*A*) was next exhausted with boiling toluene, leaving 82·5 grams (*B*) undissolved and on cooling overnight, 8 grams of yellow crystals (*C*) separated from the solution. These were extracted with 200 c.c. of 50 per cent. alcohol, the residue (*D*) being twice crystallised from toluene and then from methyl alcohol, until the melting point was constant.

Found, C = 63·77; H = 4·19.

$C_{18}H_{12}O_6$ requires C = 64·00; H = 4·00 per cent.

It consisted of pale yellow leaflets, soluble in alkali with yellow colour, and began to sinter at 210°, finally melting 221–222°. With lead acetate it gave a yellow precipitate, and its solution in sulphuric acid possessed a deep green fluorescence. The amount obtained was exceedingly small.

The acetyl compound, prepared in the usual manner, crystallised from alcohol in colourless needles, melting at 200–201°. The melting of this compound, and that of its acetyl compound, are practically the same as those given by Tschirch and Polacco for rhannocitrin and acetylrhannocitrin respectively, and the fact that its sulphuric acid solution is strongly fluorescent left no doubt as to its identity. Tschirch and Polacco adopted the formula $C_{13}H_{10}O_3$ (C = 63·44; H = 4·06), and, curiously enough, tested for the presence of a methoxy-group, with a negative result. Feeling far from certain on this point, experiments were carried out by Zeisel's method, with the result that this statement was found to be incorrect.*

Found, Me = 4·92.

$C_6H_5O_2OMe$ requires Me = 5·00 per cent.

* Manning and Nicrenstein (*Ber.*, 1913, **46**, 3983) have stated that when acetyl anhydride is employed in conjunction with Zeisel's method, a procedure not suggested as beneficial by Herzog (*Moschus*, 1889, **9**, 514), erroneous results are obtained, because hydrochloric and acetyl anhydride alone give in this way a weighable amount of silver iodide. Goldschmidt (*Ber.*, 1914, **47**, 389) has pointed out that in the case of the ordinary apparatus, where bulbs containing anhydrides of phosphorus are employed, and when pure acetic anhydride is used, this statement of Manning and Nicrenstein is incorrect. On the other hand, Goldschmidt suggests as possible that the results of these authors had been obtained with the apparatus of Perkin or of Hesse in which these bulbs are absent. Frequent practice with the former suggested as improbable that such an error occurred, but experiments were carried out with this apparatus employing pure acetic anhydride with "good

The product from the action of the hydriodic acid, which was evidently present in the form of an oxonium salt, was poured into sodium hydrogen sulphite solution, the yellow precipitate collected, crystallised from dilute alcohol, and traces of iodine still present were removed by means of potassium iodide solution. Finally, it was crystallised from acetic acid, and obtained in yellow needles, melting at 274°, which gave with sulphuric acid a fluorescent solution. The acetyl compound, prepared in the usual manner and crystallised from methyl alcohol, formed colourless needles, which melted at about 116°, gradually solidified as the temperature rose, and finally melted at 182°. Again all the properties of this colouring matter were identical with those of kaempferol, and from these results there could be no doubt that rhamnocitrin is not, as suggested by Tschirch and Polacco, an hydroxydihydroxanthone, but is in reality a monomethyl ether of kaempferol.

The only substance of this constitution at present known is the kaempferide of Galanga root, *Alpinia officinarum*, first isolated by Jahns (*Ber.*, 1881, **14**, 2385), who found its melting point to be 221--222°, and that of its acetyl derivative 188--189°. According, however, to the later work of Tiamician and Silber (*Ber.*, 1899, **32**, 861), and Testoni (*Gazzetta*, 1900, **30**, ii, 327), kaempferide and acetylkaempferide melt, respectively, at 227--229° and 193--195°, and although in general respect rhamnocitrin very closely resembles kaempferide, it would appear, more especially from the difference in the melting point of their acetyl derivatives, that they are distinct compounds. In order to compare the two compounds, an ethereal extract of Galanga root was obtained by purchase, but this proved to be of no service, in that but a trace of kaempferide was present, and further experiments could not be carried out owing to the fact that our joint work had to cease at an earlier period than had been anticipated. It is hoped, however, to subsequently deal with this matter.

The main residue (*D*), 82·5 grams, from which the rhamnocitrin had been removed, was now extracted, respectively, with boiling chloroform and boiling water, in the hope that some definite separation would be thereby effected. As this did not prove to be the case, the product was next digested with 350 c.c. of boiling alcohol, filtered [filtrate (*E*)], and the residue washed with 50 c.c. of hot alcohol. The latter, which weighed 11·5 grams, and was of

hydro-silicic acid" (*D* 1·7) alone. The results were as anticipated, no silver iodide being thus produced, from which it appears that if Manning and Nierenstein employed Perkin's apparatus their difficulties must have arisen from the use of impure acetic anhydride or of acid of a strength greater than that known as "Zeisel."

a very sparingly soluble nature, was purified by extraction with 800 c.c. of boiling acetic acid, and the solution, on cooling, deposited 3·7 grams of yellow crystals, melting at 280—282° [filtrate (*P*)]. On acetylation, colourless needles were obtained, which after re-acetylation, melted at 189°. A similar treatment of the residue not dissolved by the acetic acid indicated that this was almost entirely the same compound as the acetyl derivative melted at 190°. On hydrolysis of the latter, and subsequent re-acetylation, it was eventually obtained of the constant melting point 190—192°.

Found, C = 59·16; H = 4·09.

$C_{16}H_8O_7Ac_4$ requires C = 59·50; H = 4·13 per cent.

Hydrolysis with hydrochloric acid in the usual manner indicates the presence of four acetyl groups.

Found, $C_{16}H_{12}O_7$; 65·92.

$C_{16}H_{20}O_1$ requires $C_{16}H_{12}O_7$; 65·29 per cent.

An analysis of the colouring matter gave the following result:

Found, C = 60·55; H = 3·91.

$C_{16}H_{12}O_7$ requires C = 60·76; H = 3·79 per cent.

It consisted of yellow needles, melting above 300°, soluble in alkaline solutions with a yellowish colour, and giving with alcohol lead acetate an orange-red precipitate.

This compound agreed in general properties with the β -rhamnocitrin of Tschirch and Polacco, who give the melting point of the acetyl compound as 190—191°. The method of isolation also adopted by these authors corresponds very closely with that given in this paper, but, on the other hand, the formula $C_{15}H_{10}O_5$ which they have adopted requires C = 63·44; H = 4·06, much higher figures than those here found. Again, it was observed by these chemists that β -rhamnocitrin in some respects resembles rhamnetin, although mention is made in their paper that it is different from rhamnetin, and contains no methoxy-group. Krasowski (*loc. cit.*), however, states that he has isolated rhamnetin from the hydrolysed extract of these berries, but gives the melting point of the acetyl compound as 183—184°, which is practically identical with that given by Liebermann and Hörmann (*Ber.*, 1878, 11, 1618), 181—183°, and by Herzog (*Monatsh.*, 1888, 9, 548), 183—185°, but much lower than that of β -rhamnocitrin, 190—192°.

Examination showed that, contrary to the statement of Tschirch and Polacco, a methoxy-group is present in this substance.

Found, Me = 3·03.

$C_{16}H_8O_7Ac_4$ requires Me = 3·09 per cent.

The demethylated product proved to be quercetin, in that it had

all the properties of this substance, and gave the acetyl derivative, melting at 193—195°. (Found, C=59·69; H=3·47. $C_{15}H_{10}O_2$ requires C=59·60; H=3·31 per cent.)

In order to determine if this compound was in reality rhamnetin, or a distinct monomethyl ether of quercetin, some quantity of rhamnetin was specially prepared from Persian berries and submitted to exhaustive purification. From this the acetyl compound, obtained in the usual manner, melted at 190—192°, and was identical with that described above. It is evident, therefore, that this colouring matter of the berries of *R. catharticus* is rhamnetin, and Krasowski is correct in this respect, although his preparation cannot have been pure. On the other hand, there can be no doubt that, under the name of β -rhamnocirin, Tschirch and Polacco obtained pure rhamnetin, but the statement that their compound did not contain a methoxy-group, and their analytical results are difficult to explain.

The acetic acid liquors (*F*) produced during the purification of rhamnetin were treated with water, and the yellow precipitate, which, when dry, weighed 2·9 grams, was extracted with alcohol, and the operation repeated until all traces of the less soluble rhamnetin had been removed. The combined extracts were evaporated to dryness, and the residue acetylated, by which means an acetyl compound, melting at 190°, was isolated. By a redigestion with boiling acetic anhydride and frequent recrystallisation, this eventually melted at 193—194°. The free colouring matter (0·22 gram), obtained by hydrolysis, consisted of yellow needles, melting at 308—309°. (Found, C=59·41; H=3·49. $C_{15}H_{10}O_2$ requires C=59·60; H=3·31 per cent.) It was evidently quercetin, and Krasowski's statement in this respect is thus confirmed.

Among the compounds isolated by Tschirch and Polacco, there is none that corresponds in property with quercetin, and, indeed, the amount present in the hydrolysed berry extract is very small, and minute in comparison with the quantity of this dyestuff which can be obtained from Persian berries. The alcoholic filtrate (*E*) obtained during the isolation of the rhamnetin was treated with water, and the yellow precipitate, which, when dry, weighed 48 grams, was crystallised from 50 per cent. alcohol. It was now dissolved in alcohol, a trace of sparingly soluble substance removed, and the filtrate fractionally precipitated with water, employing quantities of the latter varying between 100 and 200 c.c., so that six distinct deposits were obtained. Of these, the first four, amounting to 27 grams, consisted almost entirely of the same substance, and this was crystallised from acetic acid until

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the melting point was constant. (Found, C=62.86; H=3.57
 $C_{11}H_{10}O_4$ requires C = 62.94; H = 3.49 per cent.)

It consisted of yellow needles, melting at 275°, soluble in alkaline solutions with a yellow coloration, and giving with alcoholic lead acetate a yellow precipitate.

The acetyl compound crystallised from methyl alcohol in colourless needles, which melted at 116°, resolidified at a higher temperature, and finally melted at 181°. (Found, C = 60.79; H = 3.93
 $C_{11}H_{10}O_6$ = 63.25. $C_{11}H_8O_6Ac_2$ requires C = 60.79; H = 3.93
 $C_{11}H_{10}O_6$ = 62.99 per cent.)

On fusion with alkali, this colouring matter gave phloroglucinol melting at 212°, and phydroxybenzoic acid, melting at 209°, and there could, accordingly, be no doubt that it consisted of kaempferol. It is quite evident that this compound represents the rhamnolutin of Tschirch and Polacco, who isolated it in a pure condition, and determined its correct formula. They, however, erred in considering that it was a new flavone colouring matter, and were evidently unaware of the production of kaempferol from kaempferide, its methyl ether, by Gordin (*Diss.*, Berne, 1897) and its isolation in the free condition by Perkin and Pilgrim (1898, **73**, 267) from the flowers of *Delphinium zulu*.

Kaempferol is by far the main constituent of the colouring matters derived from the berries of *R. catharticus*, and Krasowski, who goes so far as to deny its existence, and to criticise the work of Tschirch and Polacco in this respect, can at the most have made but a cursory examination of his product.

As to the nature of Tschirch and Polacco's rhamnochrysin $C_{11}H_{10}O_7$ (C = 56.11; H = 3.59), an opinion cannot be given, for a compound containing so low a percentage of carbon was encountered during this work. Should any substance other than those isolated have escaped detection, the amount present could be but trifling, for the accumulated residues, apart from a trace of emodin, were found to consist chiefly of impure kaempferol.

The shades given by the berries of *R. catharticus* on mordanted woollen cloth indicate that they possess much poorer dyeing properties than Persian berries. This is evident from the following table, which represents the dyeings obtained when equal weights of material were employed in each case:

	<i>Persian berries.</i>	<i>Hungarian berries.</i>
<i>Chromate</i>	Dull orange red	Dull olive yellow
<i>Glycinate</i>	Bright yellow	Pale greenish yellow
<i>Copper</i>	Dull olive yellow	Dull puce
<i>Tin</i>	Bright orange	Pale orange yellow
<i>Iron</i>	Dull olive	Pale dull olive

It has long been known that Persian berries contain a peculiar

ferment, now termed "rhamninae," which at 40° in the presence of water hydrolyses the glucosides, with separation of the free colouring matter. This change naturally occurs when the dye-bath is slowly raised to boiling point, as in the foregoing experiment, the shades obtained being due to the free colouring matter, and not to the glucosides. On the other hand, if the berries are added to boiling water, the ferment is killed, and on dyeing with such an extract, colours of a much yellower character, due to the glucosides, are produced. By experimenting in a similar manner with the berries of *R. catharticus*, it was found that, after treatment with boiling water, shades similar to those described above, but of a much paler character, were obtained, indicating, apparently, the presence of a similar enzyme in this material. For reasons given above, attempts to isolate the latter have not as yet been made.

Summary.

The colouring matters rhamnolutin, rhamnocitrin, and β -rhamnocitrin isolated from the berries of *R. catharticus* by Tschirch and Peláez consist, respectively, of kaempferol, a kaempferol methyl ether, and rhamnetin, but it is considered that their β -rhamnochrysin is not a distinct substance. The statements of Krasowski that the two former compounds cannot be isolated from these berries, and that rhamnolutin is possibly rhamnetin, whereas rhamnocitrin is exactly like quercetin and rhamnetin, are obviously incorrect, although the results of this author in regard to the presence of rhamnetin and quercetin in the mixed colouring matters have been confirmed. The latter are, however, only present in small amount, the main constituent being kaempferol, and to this the dyeing property of these berries is chiefly due.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

CXIX.—*The Methylation of Cellulose. Part II. Hydrolysis of Methylated Cellulose.*

By WILLIAM SMITH DENHAM and HILDA WOODHOUSE (Carnegie Fellow).

THE methylation of fibrous cellulose by the agency of sodium hydroxide and methyl sulphate, with the formation of products the composition of which may be represented by the simple empirical formulæ $C_{12}H_{19}O_9;OMe$ and $C_6H_9O_4;OMe$, has been

described in a previous communication (T., 1913, 103, 1735); it was there pointed out that, notwithstanding the apparent constancy in composition of the substances formed in several independent series of experiments carried out under slightly varied conditions the methylated products are nevertheless not necessarily chemically individuals. The results now communicated of additional experiments on the methylation of cellulose, and of a study of the hydrolytic decomposition of the methylated cellulose, tend to confirm the view that the latter substance is not chemically homogeneous. It is, however, important to notice that the expectation that the products of hydrolysis of the methylated cellulose would prove to be methylated glucoses has been justified; the further investigation of these methylated sugars which is now in progress will, it is hoped, afford definite evidence regarding the manner of linkage of the glucose residues in the cellulose molecule.

The well marked stages formerly observed on the first and second treatments of the cellulosic material with the methylating reagents, which corresponded respectively with the formulae $C_{12}H_{19}O_9 \cdot OMe$ and $C_6H_9O_4 \cdot OMe$, were not encountered on a repetition of the experiments with a larger quantity of material. In the following table a comparison is made of the amounts of methoxyl in the products from each successive treatment in one of the original series of experiments described in the former paper (I) with those in the products at the corresponding stages in a newer series (II), the details of which are given in the experimental part of this communication.

Concentration of sodium hydroxide,	Percentage of methoxyl after				
	1st	2nd	3rd	4th	5th treatments
I. 15-18 grams per 100 c.c.	8.5	19.7	23.3	25.5	24.6
II. 17	5.3	11.5	14.0	18.7	20.7

The divergences between the methoxyl contents at corresponding stages in the two series, due perhaps to the somewhat different concentrations of the alkali and to the differences in the quantities of material undergoing treatment, clearly indicate that the agreement previously observed between simple formulae and the composition of the methylated cellulose is fortuitous; a study of the products of the hydrolytic decomposition of methylated cellulose points to the same conclusion.

The yields at each stage of series II in the foregoing table indicated that but little of the methylated cellulose had dissolved in the wash-water, but, on repeating the process for a sixth time, a considerable quantity of material passed into solution. This may

* The percentages of sodium hydroxide quoted in the original paper are approximate and refer to grams per 100 c.c. of solution. In the later experiments the concentrations have been accurately determined.

perhaps be due to the fact that a much more concentrated solution of sodium hydroxide was employed. Both portions of the product from this final treatment—the part which remained undissolved and the part which dissolved—contained approximately the same proportion of methoxyl; it is therefore assumed, meantime, throughout the following discussion, that both possessed the same constitution.

The hydrolysis of the methylated cellulose was carried out on the undissolved portion from the final treatment, which contained about 25 per cent. of methoxyl, and was effected by the use of very concentrated aqueous hydrochloric acid, according to the method employed by Willstätter and Zechmeister for the hydrolysis of cellulose (*Ber.*, 1913, **46**, 2401). The process, which proved highly efficient, and was unaccompanied by any evidences of profound decomposition, yielded a mixture of methylated hexoses, which were separated by the methods described in the experimental part. A trimethyl hexose was obtained in the crystalline state, and there is little doubt that this compound is a true methylated glucose, since it displays practically identical specific rotation in all ordinary solvents, and this property, as already pointed out by Irvine and Hogg (this vol., p. 1386), is characteristic of the glucose configuration. The various hydrolytic products isolated may thus be classified as follows:

- (1) An amorphous monomethyl glucose, or mixture of mono-methyl glucoses.
- (2) An amorphous dimethyl glucose, or mixture of dimethyl glucoses.
- (3) A crystalline trimethyl glucose.
- (4) A trace of crystalline matter which, in crystalline form and range of solubility, resembled tetramethyl glucose.

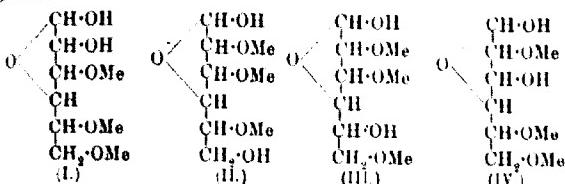
No glucose was isolated, but indications were obtained of its presence or of the presence of an unmethylated product.

In considering the significance of these products of hydrolysis, it is legitimate at this stage to leave almost out of account the possible occurrence of tetramethyl glucose, since the trace of this substance suspected to be present would have its presence explained by the assumption of even a very small degree of degradation during the operations of methylation. At the same time, it is conceivable that tetramethyl glucose may be a normal hydrolysis product of methylated cellulose, and that its origin may be traced to the existence in the cellulose complex of terminal glucose residues linked to the remainder of the molecule through the reducing group. The possibility presents itself that cellulose may consist essentially of an open chain of condensed glucose residues.

Although no very precise estimate can be made at present of the relative quantities of the various products of hydrolysis, it is probable that the amounts of dimethyl and trimethyl glucoses were nearly the same; the weight of trimethyl glucose separated in the crystalline form was approximately 10 per cent. of the weight of the crude product of hydrolysis, and the presence of more trimethyl glucose was recognised by conversion of the residual mixed sugar into the corresponding methylglucosides, which were fractionated by distillation under diminished pressure. The comparative ease with which trimethyl glucose crystallises from that portion of the hydrolysis product which possesses the solubilities characteristic of a trimethyl glucose seems to indicate that only one trimethyl glucose is present, and therefore that the cellulose molecule is symmetrical. On this basis, it would be expected that a methylated cellulose which possesses the formula $C_6H_9O_4\cdot OMe$ should yield on hydrolysis monomethyl glucose, and that alone; even without assuming the symmetry of the cellulose molecule, it is probable that a monomethyl glucose or mixture of monomethyl glucoses would be obtained from a methylated cellulose represented by the above formula. A methylated cellulose of the formula $C_{12}H_{17}O_7(OMe)_2$ would contain 25·4 per cent. of methoxyl, which is approximately the percentage in the sample of methylated cellulose hydrolysed in these experiments; it might therefore be expected, unless the linkages of the glucose residues in the cellulose molecule are to a high degree unsymmetrical, that if the methylation occurred uniformly with intermediate formation of a definite compound, $C_6H_9O_4\cdot OMe$, the methylated cellulose, which contains about 25 per cent. of methoxyl, should yield on hydrolysis nearly equal quantities of monomethyl and dimethyl glucose, and but little or none of a more highly methylated sugar; since this is not in accordance with the fact, it must be concluded, especially since there is an indication of the presence of glucose in the product of hydrolysis, that notwithstanding the care taken in attempting to ensure uniform impregnation of the cellulosic material with the solution of alkali and with methyl sulphate, the methylation did not occur uniformly, and that the agreement between simple formulae and the composition of the methylated cellulose was accidental.

The occurrence of a trimethyl glucose as essentially the most highly methylated glucose derived from methylated cellulose is of importance, since it is in harmony with the view that the proportion of free hydroxyl groups to every six carbon atoms of cellulose is three; the possible occurrence, already referred to, of terminal glucose residues containing four unsubstituted hydroxyl groups would, in the presumably large cellulose molecule, cause only a

negligible increase in the ratio of hydroxyl groups to carbon atoms. It has not yet been ascertained whether the crystalline trimethyl glucose isolated is the only one present, nor has its constitution been completely determined; it does not form an osazone, a fact which indicates the replacement by methoxyl of the hydroxyl group adjacent to the reducing group. Leaving out of consideration the dimethyl methylglucosides, there are four possible trimethyl glucoses, each of which may exist in the α - and the β form:



The allocation of formula I to the trimethyl glucose derived from methylated cellulose is excluded, since a methylated glucose represented by this formula would be able to form an osazone. The sugar of this constitution has already been prepared by Irvine and Scott (T., 1913, 103, 564), and by Irvine and Macdonald (unpublished result), and differs in properties from that under discussion. A trimethyl glucose of the constitution represented by formula II has been prepared by Irvine and Dick (unpublished), and likewise differs in properties from that derived from cellulose. There remain, therefore, formulae III and IV, a discrimination between which has not yet been attempted.

The amorphous monomethyl and dimethyl glucoses were separated by conversion of the residual syrup, from which the trimethyl glucose was extracted into a mixture of methylglucosides, which were separated by the action of solvents and by distillation. The methylglucosides were then hydrolysed. Neither of the sugars appears to be identical with methyl glucoses already known. Both form osazones. It is very probable that each is a mixture, for, even on the assumption that only one trimethyl glucose (counting the α - and β -form as one) can be obtained from methylated cellulose, the possibility occurs of three monomethyl and three dimethyl glucoses being liberated on hydrolysis as derivatives of the incompletely methylated glucose residues of the cellulose molecule. Again, if the glucose residues in cellulose are not symmetrically linked, the liberation of more than one trimethyl glucose, and of a correspondingly greater number of monomethyl and dimethyl glucoses, would be expected on hydrolysis of the methylated cellulose. It is therefore not surprising that the amorphous mono-

methyl and dimethyl glucoses, although they gave good analytical figures, could not be obtained in the crystalline state, for, on the simplest assumption, each may be a mixture of three or, counting the α - and β -forms separately, of six isomeric substances, and they may be more complex mixtures.

It remains to notice the evidence for the occurrence of glucose in the product of hydrolysis. That portion of the syrup obtained on hydrolysis which was least soluble in acetone dissolved readily and completely in methyl alcohol, so that it cannot have contained an appreciable quantity of glucose, unless (as may have been the case) the solubility of any glucose present was greatly modified by the presence of other substances. One portion of this fraction contained about half the percentage of methoxyl that would be present in a monomethyl glucose; this seemed to indicate the presence of a disaccharide, but the results of molecular-weight determinations and the percentages of hydrogen and carbon (determined in the purified, but still apparently impure, substance, a small quantity only of which was available) were not in agreement with the composition of such a compound. From the corresponding fraction derived from another portion of the same sample of methylated cellulose, a substance of approximately the same methoxyl content as monomethyl glucose was separated. It seems probable, therefore, that the product of hydrolysis contained some uncombined glucose. These results are quoted at this stage as, in utilising Willstätter and Zechmeister's method of hydrolysis, we have not ignored the possibility that, under the condensing influence of the concentrated acid used, a certain amount of autocondensation may have taken place in the liberated sugars.

The research is being extended in order to complete the methylation of cellulose and to ascertain the constitution of the methylated sugars formed on hydrolysis.

EXPERIMENTAL.

Methylation.

The methylated cellulose which was subjected to hydrolysis was prepared by impregnating cotton wool (1 equivalent $C_6H_{10}O_5$) with a solution of sodium hydroxide (2 mols.), and adding methyl sulphate in portions to the mixture until the alkaline reaction disappeared; this required about one and a-half times the quantity of methyl sulphate calculated to react with the sodium hydroxide present. The mixture became warm during the reaction, and the methylated cellulose was then washed and dried. The product from five similar consecutive treatments, in which the solution of sodium hydroxide employed contained 17 grams per 100 c.c., was

Finally (sixth treatment) soaked for a week under diminished pressure in a more concentrated solution of sodium hydroxide (38.3 grams in 100 c.c.), and then treated with sufficient methyl sulphate to destroy the alkaline reaction; this required four times the calculated quantity of methyl sulphate. In the table of quantitative details which follows, the initial weight in each case (except the first) is the quantity used of the product from the immediately preceding treatment; the final weight is that of the washed and dried product:

Concentration of the sodium hydroxide solution in 100 c.c.		
	<i>First treatment</i>	103 grams of cotton wool gave 101 grams. 0.2023 gave 0.0808 AgI. OMe - 5.28 per cent.
	<i>Second treatment</i>	99.5 grams gave 95 grams 0.3130 gave 0.2719 AgI. OMe - 11.48 per cent.
	<i>Third treatment</i>	92 grams gave 86 grams. 0.2980 gave 0.3153 AgI. OMe - 13.98 per cent.
	<i>Fourth treatment</i>	83 grams gave 79 grams. 0.3082 gave 0.4374 AgI. OMe - 18.74 per cent.
	<i>Fifth treatment</i>	74 grams gave 68 grams. 0.2719 gave 0.4258 AgI. OMe - 20.69 per cent.
	<i>Sixth treatment</i>	Concentration of the sodium hydroxide solution = 38.3 grams in 100 c.c. The methylation was carried out on two separate portions each of which was treated similarly: 65 grams gave 45.6 grams. (i) 0.2274 gave 0.4111 AgI. OMe - 23.89 per cent. 0.1655 gave 0.2986 CO ₂ and 0.1042 H ₂ O. C = 49.20; H = 7.04 per cent. (ii) 0.2315 gave 0.4550 AgI. OMe - 25.97 per cent.

The combined filtrates and washings from the sixth treatment were neutralised and evaporated on the water-bath; while the solution remained dilute, a gelatinous substance separated from the hot solution, but redissolved when the solution cooled. When the solution became more concentrated, part of the gelatinous precipitate remained undissolved in the cold solution, but redissolved when the salts present were removed by washing with water. A small portion was separated and analysed:

0.1884 gave 0.3376 AgI. OMe - 23.68 per cent.

Hydrolysis.

The methylated cellulose hydrolysed was the final product from the above operations, and contained 23.89-25.97 per cent. of methoxyl. It gelatinised when added at 0° to an aqueous solution of hydrogen chloride which had been saturated at that temperature, and dissolved in a few hours, giving a nearly colourless solution, which afterwards turned somewhat brown. The quantities used in three experiments were: (1) 12 grams of methylated cellulose and 260 c.c. of the solution of hydrochloric acid; (2) 15 grams of methylated cellulose and 650 c.c. of hydrochloric acid;

(3) 15 grams of methylated cellulose and 780 c.c. of hydrochloric acid. In each case the mixture of methylated cellulose and hydrochloric acid was allowed to remain for five to six hours at 0°, and then for twenty hours at the atmospheric temperature in a closed vessel. A current of air was now drawn through the liquid to remove part of the hydrochloric acid, and the solution then diluted. After polarimetric observations had shown that no further change was occurring, the bulk of the water and hydrochloric acid was removed by distillation under diminished pressure; the residue was diluted with water, neutralised with silver carbonate, and, after filtration, shaken with animal charcoal to remove traces of colloidal silver. The filtered solution was concentrated under diminished pressure, and yielded a nearly colourless syrup of almost exactly the same weight as the original material.

This syrup was extracted first by boiling with ether, and then by boiling repeatedly with acetone. The ethereal extract contained merely a trace of dissolved matter. The acetone extract contained trimethyl glucose, dimethyl glucose, and monomethyl glucose; it was from this fraction, also, that the trace of crystalline matter suspected to be tetramethyl glucose was separated. The residues from the extraction with ether and acetone dissolved readily in methyl alcohol; this fraction appeared to contain monomethyl glucose, and possibly glucose. It should be pointed out that the solubilities of these sugars, or rather, perhaps, the ease with which they dissolve, are greatly modified when they occur together in a mixture. Thus trimethyl glucose, which could not be extracted by ether from the crude product of hydrolysis, was found to dissolve quite readily in ether when it had been separated from the other sugars present in the acetone extract.

Acetone Extract.--The solution in acetone was concentrated, and on cooling, part of the dissolved substance was precipitated. The precipitated syrup was again extracted with acetone, and by repetitions of these operations the portion most soluble in acetone was collected; it remained as a pale yellow, very viscous syrup when the acetone was removed by distillation. A molecular-weight determination by the cryoscopic method in water showed that it consisted essentially of monosaccharides.

0·3713 gram in 8·098 grams of water gave $\Delta t = 0\cdot39^{\circ}$. M.W. 218.

Trimethyl Glucose.--This was separated from that part of the product of hydrolysis which was most soluble in acetone by adding ether to its solution in acetone. This precipitated the bulk of the dissolved matter. The supernatant liquid was decanted, the solvents removed by distillation, and the residue was redissolved in

acetone. The same cycle of operations was then repeated several times until the syrup left after distillation of the mixture and ether crystallised on keeping. The crystals were drained on a porous plate, and after several recrystallisations from ether, trimethyl glucose was obtained pure in needle-shaped crystals, melting at 110°. (Found, C=48·40; H=8·08; OMe=41·29. $C_6H_{18}O_6$ requires C=48·62; H=8·17; OMe=41·90 per cent.)

The compound at this stage was essentially the α -form. After it had been washed several times with ether it gave a maximum initial rotation:

0·1424 gram dissolved in 10 c.c. of acetone gave in a 1-dcm. tube:

	a_D	[α] _D
Initial.....	+1·44	101·12°
Final	+0·99°	68·52°

0·2678 gram dissolved in 10 c.c. of methyl alcohol gave in a 1-dcm. tube:

	a_D	[α] _D
Initial.....	+2·68°	103·98°
Final	+1·74°	67·49°

As the spontaneous changes were exceedingly slow, the equilibrium values were obtained after catalysis with a trace of sodium hydroxide. The readings were made at room temperature.

The β -form has not been isolated; it appears to be more soluble in ether than the α -form.

The ethereal mother liquors from the crystallisation of the trimethyl glucose were precipitated with light petroleum, the supernatant liquid was decanted, and the solvents were removed from it by distillation. By redissolving the residue in ether and repeating the operations just described, a trace of a crystalline substance was obtained which was soluble in light petroleum, and had the characteristic appearance of tetramethyl glucose.

Dimethyl Glucose and Monomethyl Glucose. The syrup soluble in acetone, from which trimethyl glucose had been extracted, was further worked up so as to separate the more soluble portion which, it was presumed, would contain the bulk of the dimethyl glucose. 1 Grams of this syrup were heated in a sealed tube with 80 c.c. of a 0·25 per cent. solution of hydrogen chloride in methyl alcohol for thirty-two hours, after which time the liquid no longer reduced Fehling's solution. The solution of methylglucosides was then diluted with water, neutralised with silver carbonate, and filtered; traces of silver still present were removed by warming the solution gently with animal charcoal. 5·7 Grams of a viscous, opaque, pale yellow syrup were left behind when the water was removed by

distillation under diminished pressure. The syrup was extracted repeatedly by boiling with ether. The residue from this extraction (about 2 grams) was boiled for forty-five minutes with 50 c.c. of a 5 per cent. aqueous solution of hydrogen chloride. The solution was then neutralised with silver carbonate, filtered, shaken with charcoal, and again filtered. After removal of the water, the residue was extracted with acetone, which removed very little substance, then with absolute ethyl alcohol. The material extracted by ethyl alcohol was dried in a vacuum at 60°, when it formed a hard glass, which gave analytical figures for monomethyl glucose (Found, C=43.12; H=7.29; OMe=17.09. $C_7H_{14}O_6$ requires C=43.27; H=7.27; OMe=15.99 per cent.)

0.3027 gram dissolved in 10 c.c. of methyl alcohol gave in a 1-dem. tube $\alpha_D +1.92^\circ$, whence $[\alpha]_D 63.4^\circ$.

The yellow, viscous liquid left behind when the ether was distilled from the ethereal extract obtained from the mixture of glucosides was distilled under diminished pressure. The first portion of the distillate (2.03 grams) was a colourless, viscous liquid (b. p. 141°/0.21 mm.). Its methoxyl content showed it to be a mixture of trimethyl and dimethyl glucosides:

0.1359 gave 0.4956 AgL OMe=48.18.

$C_9H_{14}O_6$ requires OMe=41.90; $C_{10}H_{20}O_6$ requires OMe=52.55 per cent.

0.2982 gram dissolved in 10 c.c. of methyl alcohol gave in a 1-dem. tube $\alpha_D +1.39^\circ$, whence $[\alpha]_D 46.61^\circ$.

The second fraction was, when cold, a colourless, transparent glass (b. p. 143°/0.03 mm.). The methoxyl content showed it to be dimethyl methylglucoside. (Found, OMe=40.57. $C_9H_{14}O_6$ requires OMe=41.90 per cent.)

0.2330 gram dissolved in 10 c.c. of methyl alcohol gave in a 1-dem. tube $\alpha_D +1.87^\circ$, whence $[\alpha]_D 80.26^\circ$.

The remainder of the second fraction was hydrolysed by boiling it for fifty minutes with 100 c.c. of a 5 per cent. aqueous solution of hydrogen chloride. The solution was neutralised with barium carbonate, the filtrate concentrated on the water-bath, and the residue dried in a vacuum at 60° and extracted with acetone; the dissolved material was dried in a vacuum, again at 60°, and again extracted with acetone. Addition of a small quantity of ether precipitated any barium chloride still present. The dried syrup finally obtained was analysed, and found to be dimethyl glucose (Found, C=46.68; H=7.89; OMe=31.26. $C_9H_{14}O_6$ requires C=46.13; H=7.75; OMe=29.81 per cent.)

0.3908 gram dissolved in 10 c.c. of methyl alcohol gave in a 1-dem. tube $\alpha_D +2.65^\circ$, whence $[\alpha]_D +67.8^\circ$.

The residue in the flask after distillation of the dimethylglucoside was a clear, brown glass—presumably monomethylmethylglucoside, but it has not yet been examined.

Residue Undissolved by Acetone.—The experimental results for this portion are given in some detail, in order to indicate the grounds for the surmise that glucose is present. The residue dissolved completely in methyl alcohol, except for a trace of colouring matter. In the case of one of the portions of methylated cellulose hydrolysed, ether was added to the solution of this residue in methyl alcohol; the precipitate, after having been dried, was re-dissolved in methyl alcohol and precipitated with acetone, when it was obtained as a soft, amorphous material, which hardened when it had been washed several times with acetone:

0·1736 gave 0·2722 CO₂ and 0·0988 H₂O. C=42·77; H=6·37.
0·1830 " 0·2870 CO₂, " 0·1075 H₂O. C=42·77; H=6·37.
0·2320 " 0·1390 AgI. OMe=7·92.

The molecular weight was determined by the ebullioscopic method in ethyl alcohol and by the cryoscopic method in water:

0·2676 gram in 15·02 grams of ethyl alcohol gave $\Delta t = 0\cdot11^{\circ}$. M.W.=186.

0·3772 gram in 22·88 grams of water gave $\Delta t = 0\cdot115^{\circ}$. M.W.=267.

A disaccharide, C₁₃H₂₄O₁₁, would require C=43·80; H=6·79; OMe=8·71 per cent. M.W.=356.

The substance was further purified by repeating several times the solution in methyl alcohol and precipitation with acetone. When dried in a vacuum at 40° it became slightly brown, and melted at 160—165°:

0·1256 gave 0·0501 AgI. OMe=5·27.

0·1398 gram in 7·99 grams of water gave $\Delta t = 0\cdot215^{\circ}$. M.W.=151·5.

The residue insoluble in acetone from the hydrolysis of another portion of the same sample of methylated cellulose was extracted repeatedly by boiling with ethyl alcohol, and the extracts were worked up so as to collect the part most soluble in ethyl alcohol. This was obtained finally as a white substance, which separated from solution in ethyl alcohol in what appeared to be a crystalline powder; when this was examined under the high power of a microscope, however, it was found to consist of minute, amorphous particles. The methoxyl content pointed to its being monomethylglucose:

0·1291 gave 0·1278 AgI. OMe=13·08.

C₇H₁₄O₆ requires OMe=15·98 per cent.

It thus appears that that portion of the product of hydrolysis

which is nearly insoluble in acetone, but soluble in methyl alcohol, and contains only half the percentage of methoxyl which would be present in a monomethyl glucose, yields a fraction which approximates in composition to a monomethyl glucose; the remainder may be glucose.

The authors would record their appreciation of the interest shown in this work by Professor Irvine.

CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

CXX.—*A Class of Salts which Contain two Solvents of Crystallisation.*

By JAMES ERNEST MARSH.

MANY halogen salts, which individually are very sparingly soluble in organic solvents, readily dissolve when two are mixed together, thereby forming a double salt. One of the two is an alkali or alkaline earth salt, and the other the salt of a heavy metal. This applies especially to the iodides, less to the bromides, and still less to the chlorides. The organic solvents in question belong to the following types: alcohols, ethers, esters, ketones, and aldehydes. Thus potassium mercuri-iodide, KI_2HgI_2 , is readily soluble in alcohol, ether, ethyl acetate, acetone, aldehyde, methylal and others although the solubility of potassium iodide and mercuric iodide separately is very slight. Frequently such double salts crystallise with the solvent. Thus we have a series of alkali-metal silver iodides with acetone of crystallisation, ammonium mercuribromide with ethyl ether, potassium mercuri-iodide with camphor, and rubidium mercuri iodide with methylal of crystallisation. In some cases, if the solvent contains water or if water is added to the solvent, a hydrated salt crystallises from the organic solvent. Examples of salts of this type are described below.

Potassium iodide and mercuric iodide in equal molecular proportions dissolve in hot methyl carbonate, and, on cooling, a salt crystallises out. The addition of one molecular proportion of water to one of the salt greatly increases the solubility of the latter, and the compound $KHgI_3 \cdot H_2O \cdot 3Me_2CO_3$ crystallizes out of cooling. If more than one molecular proportion of water is added the salt which separates is not altered in composition. As much

as ten molecular proportions of water to one of the salt have been used. The whole dissolves in hot methyl carbonate, although water alone is not appreciably soluble in this solvent. On cooling both the salt crystallises, and the excess of water separates as an aqueous solution. When a large excess of water is taken, the salt which separates is liable to be mixed with a little mercuric iodide. This is prevented by taking sufficient potassium iodide in excess to saturate the water which separates in the cold. The salt $\text{KHgI}_3 \cdot \text{H}_2\text{O} \cdot 3\text{Me}_2\text{CO}_3$ is also produced by crystallising the hydrated salt $\text{KHgI}_3 \cdot \text{H}_2\text{O}$ from methyl carbonate. When the hydrated salt is brought into contact with methyl carbonate, the clear, yellow crystals immediately begin to disintegrate, and form a nearly colourless, bulky precipitate, which dissolves very readily on warming, and the new salt then crystallises out. The salt prepared in both ways was analysed by determining the loss of weight when heated in a current of dry air. The water given off was also found by absorption with calcium chloride, and the potassium iodide, left after ignition at a low temperature, was weighed.

Found, $\text{H}_2\text{O} + \text{Me}_2\text{CO}_3 = 31.43, 31.37, 31.06$; $\text{H}_2\text{O} = 2.14$.

$\text{KHgI}_3 \cdot \text{H}_2\text{O} \cdot 3\text{Me}_2\text{CO}_3$ requires $\text{H}_2\text{O} + \text{Me}_2\text{CO}_3 = 31.72$; $\text{H}_2\text{O} = 1.98$ per cent.

The dried salt gave $\text{KI} = 26.75$; KHgI_3 requires $\text{KI} = 26.77$ per cent.

The salt begins to lose methyl carbonate on exposure to the air at the ordinary temperature. It is difficult, therefore, to guard against a slight loss of methyl carbonate during the manipulation of the crystals before weighing. It does not lose the whole of the methyl carbonate even when heated for some time at 100° , but still retains one molecule. In order to remove the whole of the methyl carbonate and the water, the salt was heated to about 160° .

The ammonium salt was prepared in a similar way. Ammonium iodide and mercuric iodide in molecular proportions dissolve sparingly in methyl carbonate, but on the addition of one molecular proportion of water, solution takes place readily, and the salt, $\text{NH}_4\text{HgI}_3 \cdot \text{H}_2\text{O} \cdot 2\text{Me}_2\text{CO}_3$, crystallises on cooling. This salt also fluoresces on exposure to air.

Found, $\text{H}_2\text{O} + \text{Me}_2\text{CO}_3 = 24.77$; $\text{H}_2\text{O} = 2.27$.

$\text{NH}_4\text{HgI}_3 \cdot \text{H}_2\text{O} \cdot 2\text{Me}_2\text{CO}_3$ requires $\text{H}_2\text{O} + \text{Me}_2\text{CO}_3 = 24.86$; $\text{H}_2\text{O} = 2.26$ per cent.

The rubidium salt, $\text{RbHgI}_3 \cdot \text{H}_2\text{O} \cdot 2\text{Me}_2\text{CO}_3$, was found to be too insoluble to dissolve in any moderate amount of the solvent. It was obtained as a crystalline powder by adding the well-crystallised salt $\text{RbHgI}_3 \cdot \text{H}_2\text{O}$ to methyl carbonate. It loses the whole of its water and methyl carbonate at about 100° .

Found, $\text{H}_2\text{O} + \text{Me}_2\text{CO}_3 = 21\cdot86$; $\text{H}_2\text{O} = 2\cdot00$.
 $\text{RbHgI}_3\text{H}_2\text{O}_2\text{Me}_2\text{CO}_3$ requires $\text{H}_2\text{O} + \text{Me}_2\text{CO}_3 = 22\cdot91$; $\text{H}_2\text{O} = 2\cdot6$
per cent.

The sodium salt was found to be so soluble that it did not crystallise until the whole solution set to a solid crystalline, yellow mass. By taking the theoretical amounts of sodium iodide, mercuric iodide, and water, the quantity of methyl carbonate required to form the dry, crystalline mass was determined. The quantities used were: sodium iodide, 2·505 grams; mercuric iodide, 7·560 grams; water, 0·296 gram; and methyl carbonate, 1·541 grams. Although no great accuracy is claimed, the result agrees with the formula $\text{NaHgI}_3\text{H}_2\text{O}_2\text{Me}_2\text{CO}_3$.

Sodium iodide and silver iodide dissolve in warm methyl carbonate in the proportion NaI to 2AgI . If less silver iodide is taken, some of the sodium iodide remains undissolved. With sufficient methyl carbonate, the solution separates into two layers. The lower layer contains nearly the whole of the salts, the upper layer only a trace. On cooling, the lower layer solidifies to a mass of crystals. The addition of water causes liquefaction and a diminution in volume of the lower layer. Further addition of water brings about a fresh separation of crystals. When sodium iodide and silver iodide are mixed with methyl carbonate and water is added, the salts dissolve in equimolecular proportions, and in these proportions the best crystallisation is obtained. When prepared in this way, the crystals have the composition $\text{NaI}.\text{AgI}.\text{H}_2\text{O}_2\text{Me}_2\text{CO}_3$.

Found, $\text{Me}_2\text{CO}_3 = 30\cdot3$; $\text{H}_2\text{O} = 6\cdot4$.
 $\text{NaI}.\text{AgI}.\text{H}_2\text{O}_2\text{Me}_2\text{CO}_3$ requires $\text{Me}_2\text{CO}_3 = 29\cdot9$; $\text{H}_2\text{O} = 6\cdot0$
per cent.

The dried salt gave $\text{AgI} = 62\cdot2$; $\text{NaI}.\text{AgI}$ requires $\text{AgI} = 61$ per cent.

The potassium salt was prepared in a similar way, and obtained in nearly colourless crystals of the formula $\text{KI}.\text{AgI}.\text{H}_2\text{O}_2\text{Me}_2\text{CO}_3$.

Found, $\text{Me}_2\text{CO}_3 = 17\cdot77$; $\text{H}_2\text{O} = 3\cdot43$.
 $\text{KI}.\text{AgI}.\text{H}_2\text{O}_2\text{Me}_2\text{CO}_3$ requires $\text{Me}_2\text{CO}_3 = 17\cdot68$; $\text{H}_2\text{O} = 3\cdot54$ per cent.
The dried salt gave $\text{AgI} = 58\cdot4$; $\text{KI}.\text{AgI}$ requires $\text{AgI} = 58\cdot5$ per cent.

I wish to acknowledge the help of a grant from the Royal Society towards the expenses of this work.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD.

CXXI.—*Interaction of Alkali Alkyl Sulphates and Alkali Nitrites: Theories of the Formation of Aliphatic Nitro-compounds.*

By PANCHANON NEOGI.

Ray and Neogi (T., 1906, **89**, 1900) have shown that nitroethane and ethyl nitrite are both produced by the interaction of alkali nitrites and alkali salts of ethylsulphuric acid. On account of the theoretical importance of the general reaction of the formation of aliphatic nitro-compounds from alkali nitrites a systematic study of the reaction with respect to other alkylsulphuric acids has been undertaken. The results show that the reaction is quite a general one, and this reopens the general question of the mechanism of the formation of aliphatic nitrites and nitro-compounds. Until lately it was known that aliphatic nitro-compounds are only produced by the interaction of silver nitrite and alkyl iodides. Ray and Neogi (P., 1907, **23**, 246), however, have shown that nitrites and nitro-compounds are both produced by the interaction of alkyl iodides and mercurous nitrite. It is now shown that nitro-compounds may be prepared by the action of alkali nitrites as well.

The formation of aliphatic nitrites and nitro-compounds is thus analogous to the formation of cyanides and isocyanides by the reaction of silver cyanide with alkyl iodide, and of alkali cyanides with the alkali salts of alkylsulphuric acids. In view of this analogy, the applicability of the theories advanced in the case of cyanides and isocyanides may be discussed with advantage in connexion with the formation of nitrites and nitro-compounds.

(a) *Tautomerism.*—Laar's idea of tautomerism seems to be scarcely applicable to nitrites and nitro-compounds. In the first place, it is indisputable that nitrous acid has the constitution HO-NO as aqueous solutions of nitrous acid with alcohols yield nitrites only and not nitro-compounds. It therefore follows that alkali nitrites and silver nitrite, formed by the action of the corresponding hydroxides on the acid, cannot possess both hydroxylie and nitro-constitutions, although Reynolds without assigning any particular reason is disposed to think that "isomeric metallic nitrites of both types exist which are also tautomeric in a marked degree" (T., 1903, **83**, 643). As regards silver nitrite, Divers (T., 1883, **43**, 455; 1885, **47**, 205) was of the opinion that it has a nitro-constitution, whilst Ray and Gaṅguli (P., 1905, **21**, 278) attempted to show that there are two varieties of silver nitrite, one obtained by precipitation and the other by careful recrystall-

lisation of the precipitated nitrite. The author has, however, found that both varieties yield the same proportion of aliphatic nitro-compounds when reacting with ethyl iodide, and agrees with Diversi (P., 1905, 21, 281), who maintained that the difference between the two is merely a physical one. With respect to mercurous nitrite Ray and Sen (T., 1903, 83, 491) think, owing to the formation of mercuric oxide in the products of the decomposition by heat, that "the atoms in some of the molecules of the nitrite arrange themselves as $Hg \cdot NO_2$, the non-oxylic form, and in others assume the oxylic form $HgO \cdot NO$, scission taking place in each case at the indicated point." It is inconceivable, however, that such a heavy atom as that of mercury would oscillate between nitrogen and oxygen in the manner suggested by Ray and Sen. Moreover, the very idea of silver, mercurous, or alkali nitrites being tautomerised runs counter to Laar's hypothesis, which is based on the mobility of the light hydrogen atom, and Wade (T., 1902, 81, 1607) well puts it in the case of silver cyanide when he says "its extension to the heavy silver atom is not justified dynamically. An atom cannot vibrate in a stable condition around a group of one-fourth of its mass."

A modified form of tautomeric explanation has been offered by Ray and Neogi (T., 1906, 89, 1905), who remark that "the more correct view would seem to be that it is only during the substitution of the atom of the metal by the alkyl radicle that a tautomeric change takes place." This argument sounds plausible, although in this case also the comparative immobility of heavy higher alkyl radicles has not been considered, and a still greater objection arises from the fact that when substitution takes place between the alkyl radicle and hydrogen in the interaction of alcohols and nitrous acid, no tautomeric change takes place, as only nitrites are formed, and no nitro-compound. It seems, therefore, that some explanation other than tautomeric change would be more suitable.

(b) *Isomeric Conversion.* — Following Gautier's hypothesis (*Compt. rend.*, 1867, 65, 468) of the possibility of isomeric conversion of cyanides and isocyanides, the isomeric conversion of nitrites into nitro-compounds at a higher temperature may be advanced as a possible hypothesis. The nitrite, of course, is formed by direct interchange as the inorganic nitrites possess oxylic constitution, and, at a higher temperature, becomes partly converted into the nitro-compound. This hypothesis has the merit of simplicity, and as the conversion would take place at a higher temperature it also explains why in the case of nitrous acid only the nitrite is obtained. The reaction between silver or mercurous nitrite and alkyl iodides takes place at 100° , and that between

alkali nitrites and alkyl sulphates at higher temperatures. Moreover, the reaction in all cases takes several hours for completion, during which time the nitrite may slowly be converted into the nitro-compound until an equilibrium is reached, although it is difficult to explain how methyl and ethyl nitrites, which are gaseous at the ordinary temperature, would be capable of such isomeric conversion. In any case, experimental evidence of the conversion of nitrites into nitro-compounds is lacking, and until such evidence is forthcoming it would be difficult to say definitely whether the hypotheses of isomeric conversion would explain the formation of nitro-compounds in all cases.

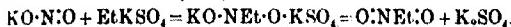
(c) *Additive Hypothesis*.—Nef (*Annalen*, 1892, **270**, 329) introduced the idea of intermediate additive compounds in the case of cyanides and isocyanides, which has been accepted and modified by Wade (T., 1902, **81**, 1596). The formation of nitro-compounds may also be readily explained on the additive hypothesis in the following manner, the nitrite being formed by direct interchange.

(i) Silver nitrite and alkyl iodides,



Mercurous nitrite behaves in a similar manner with ethyl iodide.

(ii) Alkali salts of alkylsulphuric acids and alkali nitrites:



The $\cdot\text{N}:\text{O}$ group behaves in nitrites as $\cdot\text{N}:\text{O}^-$; the alkyl group attaching itself to one of the free bonds of the nitrogen atom, and the rest of the molecule attaching itself to the oxygen. Silver and iodine, mercury and iodine, and potassium and the group KSO_4 being contiguous to each other naturally combine with each other and separate out. Experimental evidence, however, in this case also is lacking, as no such intermediate compounds have been actually isolated.

EXPERIMENTAL.

With regard to the reaction between alkali nitrites and alkali salts of alkylsulphuric acids the following general facts should be noted in connexion with the experimental results:

(1) The reaction takes place only during fusion, there being no reaction if fusion does not occur. During fusion much alcohol is produced, and the reaction may be considered to take place in the presence of the corresponding alcoholic medium.

(2) A few drops of water, when added, help the reaction by lowering the temperature at which the reaction begins, although the yield is smaller. The reaction evidently takes place in some liquid menstruum, and seems to be ionic in nature.

(3) Nitric oxide is given off in all the reactions, and is due to the

action of free sulphuric acid, obtained by the partial hydrolysis of the salts of alkylsulphuric acids, on the alkali nitrites. The potassium salt of amylsulphuric acid is the least stable of the potassium salts, and the yield of amyl nitrite is consequently the smallest, the yield of nitrite diminishing as the series is ascended.

The apparatus employed in the case of the salts of methylsulphuric acid^{*} was slightly different from what was used in the case of the salts of ethylsulphuric acid (Rāy and Neogi, T., 1924, 89, 1900). The mixture was contained in a round-bottomed flask with a short neck (instead of a glass retort), provided with a

[With BIURENDRA BHUSHAN ADHICARY.]

Alkyl sulphate. Grams.	Nitrite. Grams.	Yield of nitro-compounds. Grams.	Yield of nitrite. Grams.	Temperature at which reaction commences.	Oil obtained. Grams.
Sodium methyl...	26 Potassium	2·2-2·6	0·86	1·1	110°
Sodium methyl...	26 Sodium	2·0-2·2	0·5-0·7	105°	
Sodium methyl...	26 Barium (hydrated)	1·2	0·86	85°	
Sodium methyl...	26 Calcium (hydrated)	1·0	0·6	80°	
Potassium methyl...	30 Sodium	2·4	0·5	110°	
Potassium methyl...	30 Potassium	1·4	0·8	110°	
Potassium methyl...	30 Barium (hydrated)	1·0	0·7	80-85°	
Potassium methyl...	30 Calcium (hydrated)	1·1	0·8	80-85°	

* When the apparatus was disconnected a strong odour of methylamine was observed in the issuing gas which instantly turned red litmus blue. The formation of methylamine was probably due to the partial reduction of nitromethane by the potassium nitrite, which was already present in excess. The gas also contains ammonia, which would be due to the decomposition of hydroxylamine formed by the reduction of methyl nitrite by means of potassium nitrite. The formation of ammoniacal compounds in the case of all the methyl compounds is remarkable, as the corresponding amines were not formed in the case of the higher members of the series. It is to be noted that Wade (T., 1902, 81, 1596) also obtained the corresponding amine in the interaction of alkali cyanides and the alkali salts of alkyl sulphuric acids.

t Yield of nitro compound about 20 per cent. of the theoretical. No liquid higher boiling point as in the case of the ethyl compound.

* Kaufler and Pomeranz (*Münch.*, 1901, 22, 492) and Walden (*Ber.*, 1907, 40, 3214) have prepared aliphatic nitro-compounds by the interaction of methyl sulphide and a solution of potassium nitrite.

[With TARINI CHARAN CHOWDHURI.]

Alkyl sulphate. Grams.	Nitrite. Grams.	Yield of nitro-compounds. Grams.	Yield of nitrite. Grams.	Temperature at which reaction commences.	Oil obtained. Grams.
Potassium ethyl.....	45 Calcium (hydrated)	18	0.8-1.0	0.1-0.2	85-90 ^a
Potassium ethyl.....	45 Barium (hydrated)	30	0.8-1.0	0.2	85-90 ^a
Potassium propyl ^b ...	35 Sodium	14	2.0 (127-131°)	0.5	90 ^a
Potassium propyl ...	35 Potassium	15	2.2 (127-130°)	0.6	90 ^a 3.5
Potassium propyl ...	20 Barium (hydrated)	13	2.6	0.5-0.8	120 ^a 4.7
	Calcium (hydrated)	10			
Potassium isobutyl†	20 Sodium	8	2.6 (136-146°)	0.4 (below 75°)	135-140 ^a 3.5
Potassium isobutyl..	20 Potassium	11	2.8	0.5	135-140 ^a 4.2
Potassium isobutyl..	20 Barium (hydrated)	13	0.8	—	130 ^a 1.7
Potassium isobutyl..	20 Calcium (hydrated)	9	0.4	—	130 0.9
Potassium isooamyl..	20 Sodium	9	2.5 (150-155°)	0.9 (below 100°)	130-136 ^a 4.1
Potassium isooamyl..	20 Potassium	11	2.7	0.8	130-135 4.3
Potassium isooamyl..	20 Barium (hydrated)	11	2.2	0.4	130 ^a 4.6
Potassium isooamyl..	20 — —	2.3	0.4	—	5.5

* The oil obtained after the distillation of the residue in the case of propyl, isobutyl, and isooamyl compounds consists of a mixture of the corresponding nitrite and nitro compound, together with small quantities of the corresponding alcohol. It is difficult to separate them, and the weights given are only approximate.

† The oil obtained in the case of isobutyl, and especially amyl compounds, contains a good deal of the corresponding alcohol.

upright condenser. The flask was immersed in an oil-bath instead of a glycerol-bath. The reaction was conducted in a current of carbon dioxide, and methyl nitrite was absorbed in 90 per cent. alcohol contained in three or four Muencke's bottles immersed in ice-cold water. When the reaction was over, the liquid in the flask was distilled under diminished pressure as long as any oil passed

over, and the oily layer was separated, washed, and dried. In the case of the salts of the higher sulphuric acids, the mixture was simply heated in an oil-bath in a flask with an upright condenser and distillation was effected under the ordinary pressure up to 200°. The nitrite was estimated in alcoholic solution according to the method of the British Pharmacopoeia, and nitro-compounds were further recognized by their characteristic reaction with alcoholic sodium hydroxide, when they solidified *en masse* owing to the formation of their sodium compounds.

RAJSHAI COLLEGE, RAJSHAI, BENGAL, INDIA.

CCXXII.—Some Derivatives of *ortho*-Vanillin.*

By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

ALTHOUGH the chemistry of vanillin and piperonal has been the subject of extended investigation, largely on account of the ready accessibility of these substances, that of *o*-vanillin (I) and *o*-veratraldehyde (II)

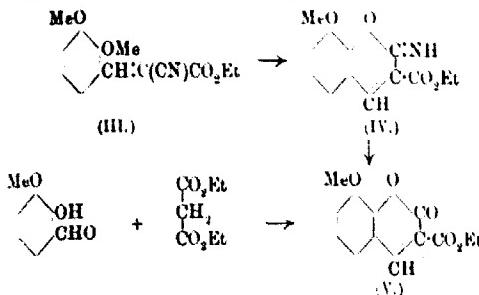


is comparatively little known, and it was partly with the view of filling this gap and partly with definite synthetical aims that the experiments described in the present communication were instituted. The following pages contain an account of the benzoic acid, benzyl alcohol, cinnamic acid, phenylpropionic acid, hydrindone, and other simple derivatives of the *o*-veratric series, and these we need not discuss in this introduction, since they were all prepared by well known methods.

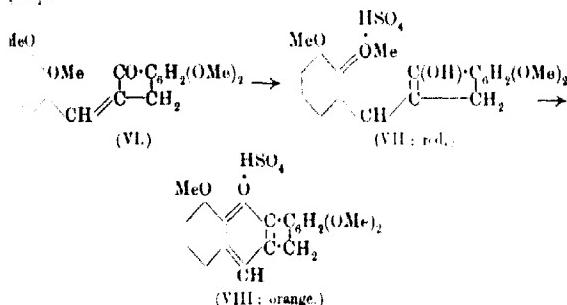
o-Veratraldehyde condenses with ethyl cyanoacetate in the presence of piperidine, with the formation of *ethyl α-cyano-2:3-dimethoxycinnamate* (III), and this is converted by the action of sulphuric acid into *ethyl 2-imino-8-methoxycoumarin-3-carboxylate* (IV), a reaction which involves the hydrolysis of a benzenoid

* Much of the experimental work described in this and the two following papers was carried out in the laboratories of Manchester University during 1910–1911. In some respects the investigations are not as complete as was intended, but as there is no immediate prospect of the subject being taken up again, it was thought best to publish the results in their somewhat incomplete form (W. H. P.; R. R.).

methoxy-group under very simple conditions, and the nature of the product seems to be proved by the fact that, on hydrolysis, it yields *2-methoxycoumarin-3-carboxylic acid*, the ethyl ester of which (V) is also produced when *o*-vanillin is condensed with ethyl malonate in the presence of piperidine (p. 2382):

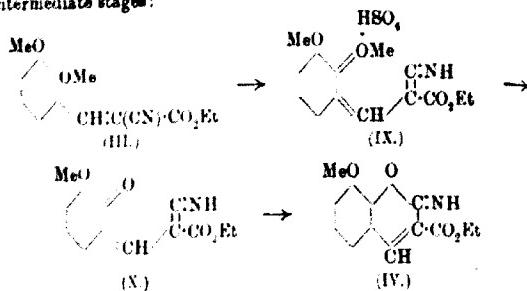


This reaction is somewhat similar to another case of the elimination of a methoxy-group which has been observed during the course of this research. 2-*o*-Veratrylidene-5:6-dimethoxy-1-hydrindone (VI, p. 2385) is obtained by condensing *o*-veratraldehyde with 5,6-dimethoxyhydrindone in the presence of alkali, and this substance dissolves in sulphuric acid to a brick red solution which contains the sulphate (VII), since it is decomposed by water with separation of the original unsaturated ketone. When, however, the red solution is allowed to remain, it soon becomes orange, and now contains the anhydro-sulphate of the pyranol base (VIII), a change which involves the elimination of a benzenoid methoxy-group.

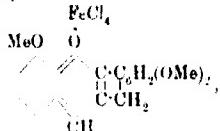


It will be seen that the *o*-quinonoid arrangement of the intermediate salt furnishes an explanation for the subsequent hydrolysis

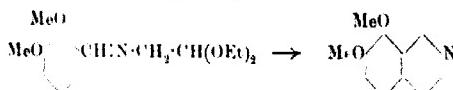
of the methoxy-group, and it does not seem improbable that a similar assumption may account for the other example of the process. In this case, the course of the reaction may be represented by the following expressions, of which the additive product of methyl hydrogen sulphate (IX) and the *o*-quinone (X) are the intermediate stages:



When 2-*o*-*vanillyl*bened-5:6-dimethoxy-1-hydrindone (p. 2385) is treated with hydrogen chloride, it yields orange crystals of the pyranol anhydro-chloride corresponding with VIII, and the anhydro-tetrachloride,



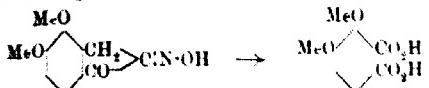
is a brick red, crystalline substance. A condensation of interest from the point of view of the synthesis of certain alkaloids is the which takes place when *o*-veratraldehyde is heated with amine-acetal, resulting in the formation of 2:3-dimethoxybenzylidene-aminoveratral, and this is converted into 6:7-dimethoxyisoquinoline by saturating the solution in 72 per cent. sulphuric acid with hydrogen chloride at 0° (p. 2382).



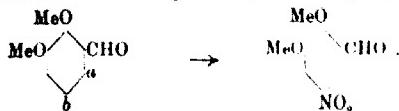
o-Veratraldehyde also condenses with glycine ester (p. 2383), but we were unable to convert the *ethyl* 2:3-dimethoxybenzylidene-aminoacetate, C₆H₃(OMe)-CH₂NH-CH₂-CO₂Et, into the corresponding isoquinoline derivative.

A synthesis of hemipinic acid was accomplished by converting

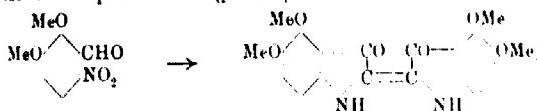
1,5-dimethoxy-1-hydrindone into the oximino-derivative (p. 2389), and then oxidising this in alkaline solution with permanganate.



Another matter of general interest arises from the study of the nitration of *o*-veratraldehyde. It will be seen that the positions *a* and *b* in the formula for this aldehyde are symmetrically placed with regard to the methoxy-groups, and it might therefore have been supposed that the aldehyde group would exercise the usual directive influence to the *m*-position, and that the hydrogen atom in the position *b* would be replaced by the nitro-group.



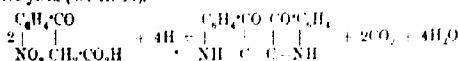
As a matter of fact, the product consists, apparently, entirely of the *o*-nitro-aldehyde, and we were unable to detect the presence even of traces of an isomeride. The ortho-position of the nitro-group was proved by the production of *tetramethoxyindigotin* by the condensation of the nitrated aldehyde with acetone in the presence of aqueous alkali (p. 2390).*



The probable explanation of this unexpected formation of the *o*-nitro-aldehyde seems to be that the negative aldehyde group neutralises the directive power of the methoxy-group adjacent to it; the second methoxy-group then directs the substitution to the para-position.

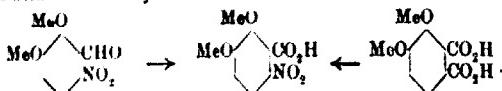
On oxidation, this aldehyde yields a nitro-acid which, from its

* An interesting method of formation of indigotin itself, which may be mentioned here (compare Eng. Pat. 16181 of 1906), consists in dissolving *o*-nitro-tetraacetic acid (Needham and Perkin, T., 1904, **85**, 154) in two parts by weight of potassium hydroxide and fifty parts of water and adding a solution of two parts of dextrose in ten of water. If this solution is gradually warmed to 50° and maintained at this temperature for ten minutes, indigotin separates apparently in almost quantitative yield (W. H. P.).



(compare Duff, this vol., p. 2182).

method of formation, can only be 6-nitro-2:3-dimethoxybenzoic acid, and this, after very careful purification, melted at 179°, and gave a methyl ester melting at 81°. Wegscheider and Kleemann (*Monatsh.*, 1910, **31**, 709), by the nitration of hemipinic acid during which a carboxyl group is replaced by the nitro-group, obtained an acid melting at 188–189° (methyl ester, m.p. 76–77°), which they regard as 6-nitro-2:3-dimethoxybenzoic acid. There is every reason to suppose, as the following scheme shows, that their view is correct, and that their acid is identical with the nitro-acid obtained by us:



but we regard their melting point for the acid as too high.

EXPERIMENTAL.

[With TSAN QUAN CHOU.]—*Ethyl α-Cyano-2:3-dimethoxy-cinnamate* (III).

o-Veratraldehyde (10 grams) and ethyl cyanoacetate (6·2 g.) were mixed and heated on the water-bath. The addition of ten drops of piperidine caused a rapid condensation, accompanied by rise of temperature, and, on cooling, the product set to a solid mass, which was dissolved in hot alcohol. The substance separates in pale yellow needles from the cooled solution, and, after recrystallisation from alcohol, melted at 120°:

0·1454 gave 0·3423 CO₂ and 0·0768 H₂O. C=64·2; H=5·8.

0·1502 " 7·3 c.c. N₂ at 16° and 756 mm. N=5·6.

C₁₄H₁₃O₄N requires C=64·3; H=5·7; N=5·3 per cent.

α-Cyano-2:3-dimethoxycinnamic Acid.

The hydrolysis of the foregoing ester was found to be best accomplished by means of a solution of hydrochloric acid in acetic acid. The cyano-ester (10 grams), acetic acid (50 c.c.), and concentrated hydrochloric acid (50 c.c.) were boiled until complete solution occurred, and then for half an hour longer, after which the yellow liquid was added to an excess of water. The bright yellow precipitate was dissolved in aqueous sodium carbonate, recovered by acidification of the filtered solution, and crystallised from glacial acetic acid. The yellow, prismatic needles so obtained were sparingly soluble in most organic solvents, and melted at 216°. The acid forms a sparingly soluble sodium and potassium salt:

0.1070 gave 0.2426 CO₂ and 0.0471 H₂O. C = 61.8; H = 4.8.

0.1376 " 7.6 c.c. N₂ at 16° and 746 mm. N = 6.3.

C₁₂H₁₁O₄N requires C = 61.7; H = 4.7; N = 6.0 per cent.

α-Cyano-2:3-dimethoxycinnamic acid can be sublimed without decomposition, and, although itself a yellow substance, it dissolves in alkalis, yielding almost colourless solutions. On boiling with aqueous potassium hydroxide it suffers hydrolysis, with separation of α-veratraldehyde, and it yields the ester described above on treatment with alcohol and sulphuric acid.

Ethyl 2-Imino-8-methoxycoumarin-3-carboxylate (IV).

Ten grams of ethyl α-cyano-2:3-dimethoxycinnamate were dissolved in 50 c.c. of concentrated sulphuric acid, and when the initial rise of temperature had subsided and the liquid had again cooled, the mixture was poured into an excess of water. The clear, yellow solution was cooled and treated with aqueous potassium hydroxide until the red colour, which appeared in those portions where the alkali was in excess, was just about to become permanent. The precipitated yellow substance was collected and crystallised from ethyl alcohol or from benzene, in either of which it is sparingly soluble in the cold. The substance melts and decomposes at 139°:

0.1477 gave 0.3411 CO₂ and 0.0692 H₂O. C = 63.9; H = 5.2.

0.1532 " 7.6 c.c. N₂ at 16° and 758 mm. N = 5.7.

C₁₃H₁₃O₄N requires C = 63.1; H = 5.2; N = 5.6 per cent.

The compound dissolves in sodium carbonate solution with a red colour, changing later to yellow.

8-Methoxycoumarin-3-carboxylic Acid and its Ethyl Ester (V).

The imino-compound just described dissolves in 10 per cent. aqueous potassium hydroxide to a red solution, which when heated on the steam-bath becomes gradually yellow, and at the same time ammonia is evolved. On acidifying with hydrochloric acid, a yellow precipitate is obtained, which crystallises from acetic acid as needles, melting at 210°, and is sparingly soluble in all solvents:

0.1252 gave 0.2762 CO₂ and 0.0444 H₂O. C = 60.1; H = 3.9.

C₁₁H₈O₅ requires C = 60.0; H = 3.6 per cent.

Ethyl Ester. — (a) This substance results when the corresponding acid is boiled for some hours with 5 per cent. alcoholic sulphuric acid. It separates from alcohol in colourless crystals, and melts at 96°:

0.1176 gave 0.2708 CO₂ and 0.0536 H₂O. C = 62.8; H = 5.0.

C₁₃H₁₂O₅ requires C = 62.9; H = 4.9 per cent.

(b) The solution of the imino-compound in sulphuric acid was diluted with water and allowed to remain during four hours. The precipitate which gradually formed was collected, crystallised from alcohol, and found to melt at 96°, and at the same temperature when mixed with the compound obtained as described under (a) and (c).

(c) *o*-Vanillin (10 grams) and ethyl malonate (10·5 grams) were heated together on the steam-bath with five drops of piperidine. After ten minutes, alcohol was added and the solution allowed to cool. The crystals were collected and recrystallised from alcohol, when they melted at 96°, and at the same temperature when mixed with an equal quantity of the substance derived from the imino-compound. (Found, C = 62·6; H = 4·9 per cent.)



A mixture of *o*-veratraldehyde (12·5 grams) and aminoacetic acid (10 grams) was heated on the steam-bath during an hour. The condensation which occurred was rendered obvious by the separation of drops of water, and the cooled product was dissolved in ether, the ethereal solution dried, and distilled. After the removal of the solvent the whole passed over at 209°/18 mm., and the yield was nearly quantitative:

0·1097 gave 0·2586 CO₂ and 0·0832 H₂O. C = 64·2; H = 8·4.

C₁₁H₁₂O₄N requires C = 64·0; H = 8·1 per cent.

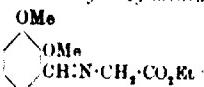
This substance was prepared in order to attempt its conversion into dimethoxy-*o*-quinoline (Rügheimer and Schön, *Ber.*, 1909, **42**, 2374, also attempted this, but without success), but the results of these experiments were very disappointing as far as the yield obtained was concerned. The base was, however, isolated in the form of its picrate.

2:3-Dimethoxybenzylideneaminoacetal was dissolved in four times its weight of 72 per cent. sulphuric acid previously cooled to 0°. The solution was then saturated with hydrogen chloride and maintained below 0° during ten days, and at the room temperature for three further days, after which the product was mixed with powdered ice. The solution was extracted with ether in order to remove small quantities of neutral substances, then rendered strongly alkaline, and again extracted with ether. The ethereal solution was dried, evaporated, and the oily residue, which could not be crystallised, converted into the picrate, which crystallised

from methyl ethyl ketone in yellow prisms. (Found, N=13.1.
Calc., N=13.3 per cent.)

The base recovered from this picrate by treatment with sodium hydroxide possessed the characteristics of *isoquinoline* derivatives, and was unchanged by treatment with boiling concentrated hydrochloric acid.

Ethyl 2:3-Dimethoxybenzylideneaminoacetate,



In effecting a condensation between glycine and *o*-veratraldehyde, it was found necessary to employ the free ethyl ester of the amino-acid, which was prepared by the decomposition of the ester hydrochloride by silver oxide in presence of ether.

Equimolecular quantities of *o*-veratraldehyde and glycine ethyl ester were warmed together on the steam-bath during two hours. The product could not be purified either by crystallisation or distillation, but an approximate analytical result was obtained from a specimen treated as follows. The crude product was dissolved in pure ether and washed with a solution of sodium hydrogen sulphite to remove any unchanged aldehyde, and then with very dilute hydrochloric acid to remove glycine ester. The dried solution was then evaporated, and the oily residue exposed to sulphuric acid in a vacuum desiccator:

(1) 1086 gave 0.2476 CO₂ and 0.0698 H₂O. C=62.1; H=7.1.

C₁₃H₁₇O₄N requires C=62.1; H=6.7 per cent.

Numerous attempts were made to induce this substance to yield a cyclic base or *isoquinoline*, but without success. The explanation of the failure is to be found in the ready hydrolysis of the condensation product, and for this reason it was also not possible to prepare the acid corresponding with the ester. In experiments, made with this object, *o*-veratraldehyde was always produced.



With WALTER MORRELL ROBERTS,]—*o*-*Veratric Acid,*

Although derivatives of this substance have been frequently described, the acid itself has apparently not been characterised, and we therefore prepared it by oxidation of *o*-veratraldehyde. The aldehyde was dissolved in acetone and treated at the room temperature with a solution of potassium permanganate (3 per cent.) until a permanent pink colour was produced. The solution

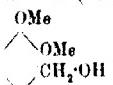
was heated, filtered, concentrated, and acidified with hydrochloric acid. The colourless, crystalline precipitate was collected and recrystallised from hot water, in which the acid is far more soluble than veratric acid itself. It separated in fern-like aggregates of prisms, melting at 122°.

0.1208 gave 0.2617 CO₂ and 0.0694 H₂O. C=59.1; H=5.6.

C₉H₁₂O₄ requires C=59.3; H=5.5 per cent.

Methyl Ester.—This compound, the first stage in Fritsch's synthesis of mecamine (Annalen, 1898, **301**, 356), had been previously obtained by the methylation of guaiacolcarboxylic acid. We prepared it by boiling *o*-veratric acid with 5 per cent. methyl alcoholic sulphuric acid, and found that it melts, as stated by Fritsch, at 47°.

*2-3-Dimethoxybenzyl Alcohol (*o*-Homoveratryl Alcohol).*



Two methods were employed in preparing this substance:

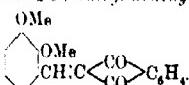
(a) *o*-Verataldehyde (10 grams) dissolved in a mixture of alcohol (250 c.c.) and water (100 c.c.) was gradually treated with 3 per cent. sodium amalgam (150 grams), with constant stirring. The solution was acidified and distilled in a current of steam, and the residue remaining in the flask extracted with ether, the ether solution dried, and evaporated. The oily residue gradually solidified, and was recrystallised from a concentrated solution in ether, from which it separated in colourless prisms, melting at 46–48°.

0.1183 gave 0.2791 CO₂ and 0.0765 H₂O. C=64.0; H=7.2.

C₉H₁₂O₃ requires C=64.3; H=7.1 per cent.

(b) *o*-Verataldehyde was boiled with 20 per cent. potassium hydroxide solution for several hours, and the cooled liquid extracted with ether. After washing the extract with sodium hydrogen sulphite solution, it was dried and evaporated, and the residue allowed to crystallise. The crystals obtained were identical with those produced as in (a). The alkaline solution on acidification yielded *o*-veratric acid.

*1: 3-Diketo-2-*o*-veratrylidenehydrindene,*



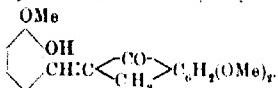
In order to prepare this substance, equimolecular proportions of 1:3-diketohydrindene and *o*-verataldehyde were cautiously

heated together until water ceased to be produced. Alcohol was then added, and the brownish crystals were collected and crystallised from acetic acid. The bright yellow needles thus obtained melted at 160° , and were very sparingly soluble in alcohol:

$\text{D}10816$ gave $0\cdot2190 \text{ CO}_2$ and $0\cdot0347 \text{ H}_2\text{O}$. C = 73·2; H = 4·7.
 $\text{C}_{18}\text{H}_{14}\text{O}_4$ requires C = 73·5; H = 4·8 per cent.

The substance dissolves in sulphuric acid to an orange solution, and is recovered unchanged on the addition of water. This observation goes to show that, in the case of the elimination of a methyl group, which is described below, it is the tendency to produce the anhydropyranol ring which is mainly operative. Where, as in the present case, this tendency is absent, then the sulphuric acid alone in the cold is not able to hydrolyse the methoxy group.

2-o-Vanillylidene-5:6-dimethoxy-1-hydrindone,

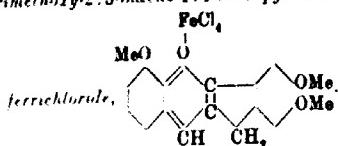


This substance was obtained when *o*-vanillin (5 grams) and 5:6-dimethoxyhydrindone (5 grams), together with potassium hydroxide (4 grams), were boiled in methyl alcoholic solution (50 c.c.) during half an hour. The liquid was then acidified with acetic acid, and the sparingly soluble yellow precipitate recrystallised from *isoamyl* alcohol. The substance forms yellow rhomboids, very sparingly soluble in most solvents, and melting at 205° . It dissolves in alkalis, yielding red solutions:

$\text{D}1125$ gave $0\cdot2882 \text{ CO}_2$ and $0\cdot0566 \text{ H}_2\text{O}$. C = 69·9; H = 5·6.
 $\text{C}_{19}\text{H}_{18}\text{O}_4$ requires C = 69·9; H = 5·5 per cent.

2-o-Veratrylidene-5:6-dimethoxy-1-hydrindone (VI) is formed when equal quantities of *o*-veratraldehyde and of 5:6-dimethoxyhydrindone, dissolved in warm alcohol, are treated with a few drops of concentrated potassium hydroxide, when in a short time the condensation product separates as a crystalline mass. The substance was collected and recrystallised from methyl alcohol, and so obtained in very pale yellow needles, melting at 186° :

$\text{D}1274$ gave $0\cdot3289 \text{ CO}_2$ and $0\cdot0688 \text{ H}_2\text{O}$. C = 70·4; H = 6·0.
 $\text{C}_{20}\text{H}_{20}\text{O}_5$ requires C = 70·6; H = 5·9 per cent.

8,4'-5'-Trimethoxy-2:3-indeno-1:4-benzopyranol Anhydro-

This interesting substance was obtained in the following different ways:

(a) Five grams each of *p*-vanillin and 5:6-dimethoxyhydrindone were dissolved in glacial acetic acid, and the solution saturated at the room temperature with hydrogen chloride. Orange crystals of the pyranol anhydro-hydrochloride separate after some time, and these were collected, dissolved in hot dilute hydrochloric acid, and converted into the ferrichloride by the addition of an excess of ferric chloride dissolved in concentrated hydrochloric acid. The precipitated brick red substance was collected and crystallised from a large volume of acetic acid, in which it is very sparingly soluble, and from which it separated in deep red prisms, melting at 240°.

0.1001 gave 0.1645 CO₂ and 0.0318 H₂O. C = 44.8; H = 3.5.

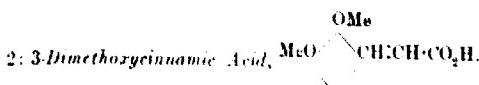
C₁₉H₁₄O₆FeCl₃ requires C = 45.1; H = 3.4 per cent.

In view of the intense fluorescence exhibited by the corresponding salt from *p*-methoxysalicylaldehyde and dimethoxyhydrindone it is interesting to note that the above isomeric ferrichloride is non-fluorescent in aqueous, or even in concentrated, sulphuric acid solution.

(b) 2-*o*-Vanillylidene-5:6-dimethoxy-1-hydrindone (see above) yields with cold concentrated hydrochloric acid a brick-red hydrichloride, which is decomposed by water, with the formation of the original unsaturated ketone. If, however, the substance is boiled with hydrochloric acid, the brick red is replaced by an orange solution, and the addition of ferric chloride in excess now precipitates the above oxonium ferrichloride, melting after crystallisation from acetic acid at 240°.

(c) 2-*o*-Veratrylidene-5:6-dimethoxy-1-hydrindone dissolves in sulphuric acid to a red solution, which rapidly becomes orange. This colour change corresponds with the production of the cyclo-oxonium salt by the elimination of a methoxy-group, and on the addition of water the whole of the substance remains in solution. For purposes of characterisation, an excess of ferric chloride dissolved in hydrochloric acid was added, and the precipitated double salt collected and crystallised from acetic acid. The deep red prisms melted at 240°, and were identical in all respects with the

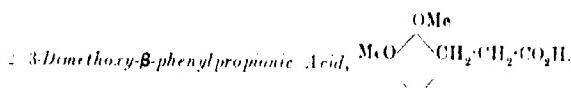
substance as obtained according to (a) or (b). This elimination of a methyl group at such a low temperature may be taken as supporting the view that the red, unsaturated ketone salts are quinonoid.



This acid is best obtained by the hydrolysis of its ester, which in its turn results from the condensation of *o*-veratraldehyde and methyl acetate by means of sodium. We have also obtained it by means of the Perkin synthesis and by Knoevenagel's method.

o-Veratraldehyde (20 grams) dissolved in ethyl acetate (50 grams) was poured on granulated sodium (5 grams), and the flask carefully cooled in order to moderate the vigorous reaction which ensued. When the action had slackened, the mixture was warmed in the steam-bath for a few minutes, and then allowed to cool. An excess of methyl-alcoholic potassium hydroxide was now added, and the solution boiled, after which the product was diluted with water, and the liquid concentrated on the steam bath. The acid was precipitated from the alkaline solution by means of hydrochloric acid, collected and crystallised first from acetic acid, and then from ethyl acetate, and was thus obtained in magnificent glistening needles, melting at 180°. It is sparingly soluble in water and most organic solvents:

'01269 gave 0'2944 CO₂ and 0'0660 H₂O. C 63'4; H 5'8.
C₁₁H₁₂O₄ requires C 63'5; H 5'8 per cent.



In preparing this acid, it was found very necessary to start with the corresponding cinnamic acid in a high state of purity.

A solution of 2: 3-dimethoxycinnamic acid (10 grams) in dilute aqueous sodium hydroxide (200 c.c.) was reduced by means of 1 per cent. sodium amalgam (300 grams). The liquid was mechanically stirred during this operation, and the end-point of the reaction could be easily determined by means of the permanganate test. The solution was carefully acidified by the addition of hydrochloric acid, and the precipitated acid collected and crystallised from a mixture of benzene and light petroleum (b. p.

50--60°, from which it separated in colourless prisms, melting at 69--70°.

0.1145 gave 0.2723 CO₂ and 0.0730 H₂O. C=62.7; H=6.8
C₁₁H₁₄O₃ requires C=62.9; H=6.7 per cent.



In preparing this substance, 2:3-dimethoxy- β -phenylpropionaldehyde (30 grams) dissolved in benzene (250 c.c.) was gently heated on the steam bath with phosphoric oxide (100 grams) during one and a half hours. The mass acquires a deep bluish-crimson colour, and this appears to be due to the formation of an additive product of the ketone and phosphoric oxide. The whole was decomposed with ice, the mixture extracted with ether, the ethereal solution washed with dilute aqueous sodium hydroxide, dried, and evaporated. The residue was an oil, which quickly solidified, and after contact with porous porcelain to remove oily impurities, the substance crystallised readily from light petroleum, or, better, from a concentrated solution in pure dry ether. It crystallises in very pale yellow plates, melting at 82°, and is readily soluble in organic solvents, with the exception of light petroleum:

0.1166 gave 0.2945 CO₂ and 0.0683 H₂O. C=68.9; H=6.5
C₁₁H₁₄O₃ requires C=68.8; H=6.3 per cent.

The properties of this substance are very similar to those of the isomeric *o*-dimethoxyhydrindone (Perkin and Robinson, T. 1907, 91, 1080), and, like the latter, it condenses very readily with aldehydes, etc.

The *benzylidene* derivative, C₆H₅(OMe)₂^{CO}>C:CHPh, readily obtained by dissolving equal amounts of the hydrindone and of benzaldehyde in warm methyl alcohol, and adding a few drops of concentrated aqueous potassium hydroxide. In a few minutes the derivative separates, and after recrystallisation from alcohol melts at 166--167°. It crystallises in pale yellow needles which are sparingly soluble in cold alcohol, and dissolve in sulphuric acid to a red solution:

0.1139 gave 0.3200 CO₂ and 0.0578 H₂O. C=76.6; H=5.4
C₁₁H₁₄O₃ requires C=77.1; H=5.7 per cent.

The *anisylidene* derivative, C₆H₅(OMe)₂^{CO}>C:CH-C₆H₄OMe is obtained by replacing benzaldehyde by anisaldehyde in the above preparation, and consists of feathery needles, melting at 134

This pale yellow compound exhibits intense haloehromism, and becomes brick-red in contact with concentrated aqueous hydrochloric acid:

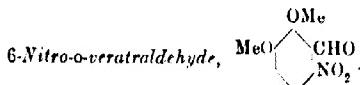
$\text{C}_{12}\text{H}_{10}$ gave 0.3235 CO₂ and 0.0634 H₂O. C = 73.3; H = 5.9.
 $\text{C}_{19}\text{H}_{18}\text{O}_4$ requires C = 73.6; H = 5.8 per cent.

The *oximino-derivative*, $\text{C}_6\text{H}_5(\text{OMe})_2 <\text{CH}_2>\text{C}=\text{NOH}$, was prepared as follows. The hydrindone (10 grams), mixed with methyl alcohol (30 c.c.), concentrated hydrochloric acid (5 c.c.), and freshly distilled *isoamyl nitrite* (15 grams), was maintained at about 50° during an hour. The crystals of the oximino-derivative, which separated in almost quantitative yield, were collected and recrystallised from alcohol, and were so obtained in yellow needles, melting and decomposing at 244°. The substance dissolves to a yellow solution in alkaline hydroxides, or even in sodium carbonate:

C_{11}H_9 gave 0.2498 CO₂ and 0.0526 H₂O. C = 59.6; H = 5.1.
 C_{11}H_9 " 70 c.c. N₂ at 21° and 751 mm. N = 6.9.
 $\text{C}_{11}\text{H}_9\text{O}_4\text{N}$ requires C = 59.7; H = 5.0; N = 6.3 per cent.

Oxidation of the Oximino-derivative: Formation of Hemipinic Acid.

For the purpose of this oxidation, 5 grams of the substance were dissolved in the least possible amount of sodium hydroxide, four c.c. of water were added, and the solution was treated at the same temperature with saturated aqueous potassium permanganate until a permanent pink colour was obtained. The liquid, to which a few drops of alcohol had been added, was then boiled, filtered, concentrated to a small bulk, acidified, saturated with ammonium sulphate, and repeatedly extracted with ether. The combined extracts were dried, filtered, and evaporated, and the residue was distilled in a stream of ammonia. In this way a quantity of a crystalline distillate was obtained, and this was collected and crystallised from alcohol, when colourless needles separated, and were identified as hemipiminide, since they melted at 229°, and the melting point was unaltered when the substance was mixed with an equal quantity of hemipiminide obtained by the action of hydroxylamine hydrochloride on a boiling alcoholic solution of pionic acid.

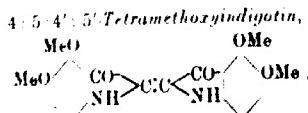


In preparing this derivative, *o*-veratraldehyde was added, with careful cooling, to ten times its weight of nitric acid (D 1.42), the

solution allowed to remain during five minutes, and then diluted with water. The precipitated nitro-aldehyde was collected and crystallised from methyl alcohol, from which it separated in very pale yellow needles, melting at 88°. Neither nitro- nor dimethoxyveratrole could be detected as a by-product of this nitration:

0.1137 gave 6.6 c.c. N₂ at 22° and 752 mm. N = 6.6.

C₉H₁₀O₂N requires N = 6.6 per cent.



The formation of this compound has particular interest, inasmuch as it demonstrates that the product of the nitration of *o*-veratraldehyde is the *o*-nitro-aldehyde.

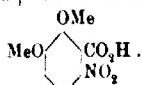
In order to obtain this substituted indigotin, aqueous potassium hydroxide (5 c.c. of 10 per cent.) was gradually added during 5 minutes to a solution of nitro-*o*-veratraldehyde (2 grams) in acetone (10 c.c.). The brownish-red liquid was then mixed with water (100 c.c.) and heated during an hour on the steam-bath. The indigotin derivative was collected, and in this condition had a slaty appearance, but after crystallisation from acetic anhydride, or, better, aniline, it was obtained in needles having the characteristic appearance of indigotin, and melting at 267° with partial decomposition and partial sublimation:

0.1085 gave 7.2 c.c. N₂ at 18° and 752 mm. N = 7.7.

C₁₆H₁₂O₄N₂ requires N = 7.3 per cent.

Tetramethoxyindigotin behaves as a vat dye, and is readily oxidised by nitric acid, but we were unable to isolate the corresponding isatin derivative.

[With DAVID CARDWELL.]—6-Nitro-2:3-dimethoxybenzoic Acid

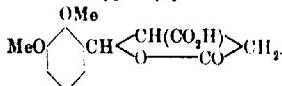


The position taken up by the nitro-group in the nitration of *o*-veratraldehyde appeared to us so very curious that we were anxious to determine whether or no an isomeric compound was formed at the same time. The crude nitro-aldehyde was therefore oxidised by means of warm permanganate in the presence of sodium carbonate until the colour was no longer discharged. After the excess had been destroyed by alcohol, the solution was concen-

gated and acidified, and the precipitated acid collected. The crude nitro-acid (10 grams) was dissolved in methyl-alcoholic hydrogen chloride (75 c.c. of 3 per cent.), and allowed to remain for forty-eight hours at the room temperature. Under these conditions, only a small proportion of the acid was esterified, since, on the addition of water, a precipitate almost completely soluble in dilute sodium carbonate solution was obtained. It might have been expected that the small residue would consist of methyl 1 or 5-nitro-2:3-dimethoxybenzoate, either of which should be more readily obtained by esterification than the 6-nitro-isomeride; but on crystallisation the substance was obtained in colourless needles, melting at 81°, and at the same temperature when mixed with the ester obtained as described below. The unesterified acid was recovered from the alkaline solution by acidification, and crystallised several times from water, and then from ethyl acetate, and was thus obtained in colourless needles, melting at 179°. The solution of 6-nitro-2:3-dimethoxybenzoic acid in hot water or in alkalis is yellow, and this appears to be a case to which the Ostwald theory of indicators may correctly be applied. (Found, C = 47·6; H = 3·8. Calc., C = 47·6; H = 3·9 per cent.)

The methyl ester was prepared by boiling the acid with 10 per cent. methyl-alcoholic sulphuric acid for several hours, and was purified by crystallisation from methyl alcohol, from which it separated in colourless needles, melting at 81°. (Found, C = 49·9; H = 4·5. Calc., C = 49·8; H = 4·6 per cent.)

2:3-Dimethoxyphenylparaconic Acid,



In the preparation of this acid, equimolecular quantities of veratraldehyde, anhydrous sodium succinate, and acetic anhydride were maintained at 125° during three and a-half hours. The product was then boiled with water, and neutralised by the gradual addition of sodium carbonate, the hot solution was filtered from the tar which is always formed in considerable quantity, boiled with animal charcoal, filtered, and acidified with hydrochloric acid. The paraconic acid separated gradually from the solution in colourless needles, which, after crystallisation from formic acid or aqueous acetic acid, melted at 132°. The yield was only about 20 per cent. of the theoretical:

1243 gave 0·2665 CO₂ and 0·0624 H₂O. C = 58·5; H = 5·5.

C₁₅H₁₄O₆ requires C = 58·6; H = 5·2 per cent.

The Nitro-derivative.—Ten grams of the paraconic acid dissolved in 25 c.c. glacial acetic acid were gradually treated with NO_2 , and (25 c.c., D 1.42), with constant stirring and cooling. After remaining for several hours, water was added, and the precipitated acid collected and crystallised from 50 per cent. acetic acid, from which the substance separates in pale yellow needles, which melt at 203°.

0.1385 gave 5.9 c.c. N_2 at 18° and 769 mm. $\text{N} = 4.8$.

$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{N} = 4.5$ per cent.

It is clear that the nitro-group in this acid occupies the 6 position, since 6-nitro-2,3-dimethoxybenzoic acid was obtained as a result of its oxidation by means of potassium permanganate in alkaline solution at 9°.

The methyl ester of the nitro-acid was prepared by boiling the acid with an excess of 5 per cent. methyl-alcoholic sulphuric acid; it crystallises from methyl alcohol in colourless needles melting at 125°, and is sparingly soluble in cold alcohol:

0.2203 gave 0.1018 CO_2 and 0.0925 H_2O . $\text{C} = 51.4$; $\text{H} = 4.7$.

$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C} = 51.6$; $\text{H} = 4.6$; $\text{N} = 4.3$ per cent.

Several attempts were made to reduce this substance to the corresponding amino-derivative, which was required in connection with our experiments on harmaline and harmin, but although there were indications, in several cases, that a carbostyryl derivative had been produced from this amino-derivative by internal condensation we were unable to isolate the substance in a pure state.

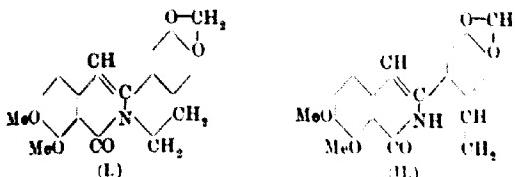
We wish to state that much of the expense of this investigation was met by several grants from the Research Fund of the Chemical Society, and to express our gratitude for this assistance.

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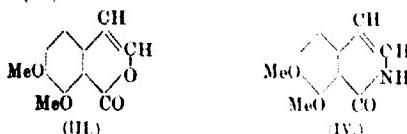
CCXXXIII.—*Some Derivatives of isoCoumarin and isoCarbostyryl.*

By DAVID BAIN, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

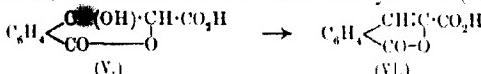
In a communication published a short time since (Bland, Perkin, and Robinson, T., 1912, 101, 262), it was shown that oxyberberine (I), when heated with dilute hydrochloric acid, is converted by a remarkable change into *iso*oxyberberine (II).



This formula for *isoxyberberine* represents that substance as derivative of *isocarbostyryl*, and, in order to further study the properties of substances of this class, it became necessary to attempt the synthesis of dimethoxy*isocoumarin* (III) and dimethoxy*isocarbostyryl* (IV) and their derivatives.



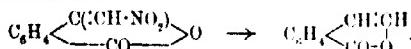
Isocoumarin (VII) has been prepared from β -naphthaquinone by oxidation with bleaching powder, when the lactone of *a*-carboxyphenylglyceric acid (V) results, and this, when heated with hydrochloric acid, is converted into *isocoumarincarboxylic acid* (VI).



The silver salt of the latter acid decomposes on distillation into coumarin and carbon dioxide, and *isocarbostyryl* (VIII) is obtained from *isocoumarin* by the action of alcoholic ammonia.

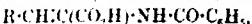


Compare Bamberger and Kitschelt, *Ber.*, 1892, **25**, 892; Bamberger and Frew, *Ber.*, 1894, **27**, 297; Zincke, *Ber.*, 1892, **25**, 1495. Coumarin has also been obtained in small quantity by Gabriel (*Ber.*, 1903, **36**, 573) from nitromethyleneephthalide by boiling with hydriodic acid.

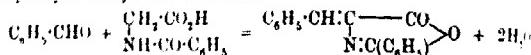


These methods are inconvenient, and have the disadvantage that they are not readily applicable to the preparation of derivatives of *isocoumarin* and *isocarbostyryl*, and, as no other means for obtaining these substances has been devised, very little work has been done in connexion with this interesting group of substances.

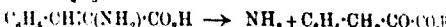
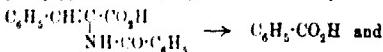
In the present communication, a method of synthesis of *isocoumarin*, *isocarbostyrol* and their derivatives is described which should be widely applicable, and depends on the hydrolysis of condensation products of *o*-aldehydo-acids and hippuric acid. Erlenmeyer, jun. (*Ber.*, 1900, **33**, 2040; *Annalen*, 1904, **337**, 25) compare Plochl, *Ber.*, 1883, **16**, 2815), has shown that, although hippuric acid does not seem capable of yielding an anhydride by internal elimination of water, the acids of the formula



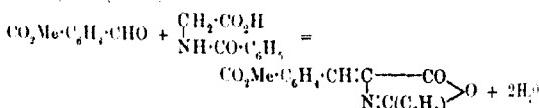
which result from the condensation of hippuric acid with aldehydes, are not obtained as such, but as anhydrides, when acetic anhydride is employed as the condensing agent. Thus, for example, when a mixture of benzaldehyde and hippuric acid is heated with acetic anhydride, the substance which crystallises from the product is 2-phenyl-4-benzylideneoxazolone,



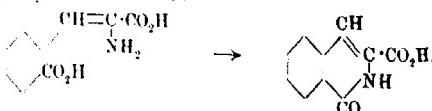
The hydrolysis of 2-phenyl-4-benzylideneoxazolone leads, in the first place, to benzylidenehippuric acid, and this decomposes, on boiling with hydrochloric acid, into benzoic acid, ammonia and phenylpyruvic acid, a process which may be represented thus:



We have investigated the condensation of methyl phthalaldehyde with hippuric acid in the presence of sodium acetate and acetic anhydride, and obtained, in this way, 2-phenyl-4-carboxymethylbenzylideneoxazolone:



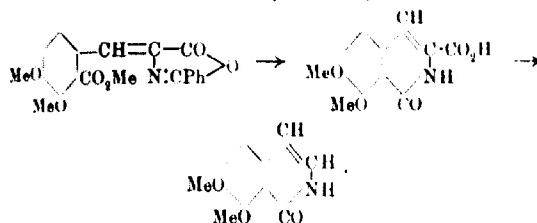
When this methyl ester is hydrolysed with potassium hydroxide it does not behave like 2-phenyl-4-benzylideneoxazolone to yield a derivative of phenylpyruvic acid, but the intermediate amino-acid loses water and is converted into the lactam, and *isocarbostyrolcarboxylic acid* is formed:



It seems clear that this difference will be observed in the case

the hydrolysis of all derivatives of 2-phenyl-4-benzylidene-azalone which contain a carboxyl group in the *o*-position with respect to the group, -CH₂C₆H₅, and the above method should therefore prove to be of general application for the preparation of derivatives of isocarbostyryl.

We have employed this method for the preparation of *S*-dimethoxyisocarbostyryl (IV), from which, as shown on p. 333, *isoxyberberine* is derived. In carrying out this synthesis, ethyl opianate was condensed with hippuric acid in the presence of acetic anhydride and sodium acetate, and the resulting 2-phenyl-carboxymethyl-*mp*-dimethoxybenzylideneazalone was hydrolysed to 7:8-dimethoxyisocarbostyryl-3-carboxylic acid. When this acid was heated it yielded a crystalline substance melting at 233°, which is doubtless 7:8-dimethoxyisocarbostyryl:



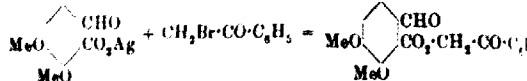
An unfortunate fire which occurred in the Laboratories of the University of Sydney destroyed the whole of the preparations made during this investigation, and before this substance and some others had been sufficiently examined and analysed. It is our intention again to prepare these and other similar derivatives of carbostyryl, and to submit them to extended investigation. The present communication contains an account of the synthesis of ethyl opianylacetate from silver opianate and ethyl bromoacetate, and this substance was prepared in the hope that it might prove possible to effect internal condensation between the aldehyde and the methylene groups, and so obtain 7:8-dimethoxyisocoumarin-carboxylic acid, which should yield 7:8-dimethoxyisocarbostyryl-carboxylic acid on treatment with ammonia:



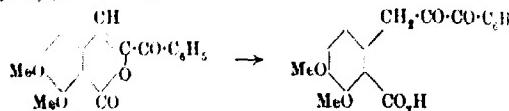
If we were unsuccessful in our attempts to bring about internal condensation,

On the other hand, a similar condensation is readily brought

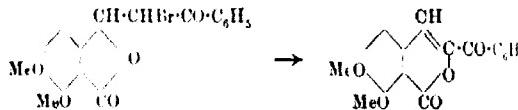
about in the case of ω -opianoylacetophenone. This substance is produced (p. 2400) when silver opianate is boiled, in benzene solution, with ω -bromoacetophenone,



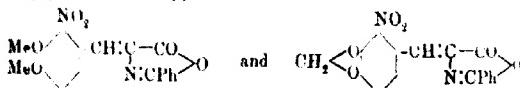
and when this is treated with alkaline condensing agents it yields, in the first place, 3-benzoyl-7:8-dimethoxyisocoumarin; a substance which is readily hydrolysed by the further action of alkali to *6 phenylglycylmethylesteric acid*:



Although ω -opianoylacetophenone is produced when silver opianate reacts with ω -bromoacetophenone, it is remarkable that an entirely different reaction takes place when the potassium salt of opionic acid is treated with ω -bromoacetophenone in the presence of potassium carbonate, and leads to the formation of ω -benzylbromomethylsuccinic acid, which, on treatment with alkali, yields 3-benzoyl-7:8-dimethoxyisocoumarin (compare p. 2401):



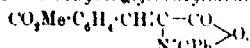
During the course of these experiments, we have also investigated the condensation of some nitro-aldehydes with hippuric acid, since it seemed likely that the substances produced might be serviceable in connexion with synthetical experiments in the alkyd group on which we are engaged. In the experimental part of this communication (p. 2403) we describe 2-phenyl-4-oxo-mp-dimethoxybenzylidenecrotonaldehyde, produced by the condensation of ω -nitrovaleraldehyde with hippuric acid, and 2-phenyl-4-oxo-mp-methylenedimethoxybenzylidenecrotonaldehyde, by the condensation of nitropiperonal with hippuric acid:



The study of the hydrolysis of these substances is not yet complete.

EXPERIMENTAL.

2-Phenyl-4-o-carboxymethylbenzylideneoxazolone,



In preparing this substance, methyl phthalaldehydeate (1 mol.; compare Graebe and Trümpler, *Ber.*, 1898, **31**, 375, and Racine, *Compt. rend.*, 1887, **239**, 84), hippuric acid (1 mol.), and acetic anhydride (3 mols.) were intimately mixed with fused sodium acetate (1 mol.), and heated on the steam-bath during half an hour. On cooling, the yellow liquid became almost solid, owing to the separation of crystals. Water was now added, the precipitate collected, washed, and crystallised from glacial acetic acid, from which the new substance separated in groups of yellow needles. It melts at 171°, and is very sparingly soluble in methyl or ethyl alcohols or in ether:

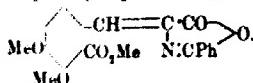
On 1246 gave 0.3192 CO₂ and 0.0454 H₂O. C = 69.9; H = 4.1.

C₁₈H₁₃O₄N requires C = 70.3; H = 4.2 per cent.

isoCarbostyrylcarboxylic Acid and isoCarbostyrd,



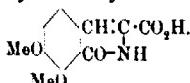
When 2-phenyl-4-o-carboxymethylbenzylideneoxazolone is heated with excess of 10 per cent. aqueous potassium hydroxide until the whole of the substance has dissolved, a red solution is obtained which, on acidifying, deposits a flocculent, microcrystalline precipitate. This was dissolved in aqueous ammonia, reprecipitated, collected, and crystallised from acetone, in which it is sparingly soluble. The slender needles so obtained melted at 320°, with some previous decomposition, and in this and other properties the substance was identified with *isoCarbostyrylcarboxylic acid* prepared by Bamberger and Kitschelt (*Ber.*, 1892, **25**, 1143). *isoCarbostyrd* was obtained from the carboxylic acid by heating the silver salt or by simply heating the acid for some time at a temperature just below its melting point. The product was purified by sublimation, after the unchanged acid had been removed by sodium carbonate solution, and melted at 208°, as stated by Bamberger and Kitschelt (*loc. cit.*, p. 1145).

*2-*p*-phenyl-4-*o*-carboxymethyl-*mp*-dimethoxybenzylideneoxazoline,*

This substance is obtained by the condensation of methyl opianate with hippuric acid (compare p. 2395). Methyl opianate has been prepared by Wegscheider (*Monatsh.*, 1882, **3**, 358; 1892, **13**, 251) by the action of methyl iodide on silver opianate, and he employed silver fluoride for the preparation of this salt, but in our experiments we have adopted the following procedure, whereby a very good yield of the pure methyl ester is obtained. A hot, concentrated aqueous solution of silver nitrate (20 grams) is added at once, and with stirring, to a hot solution of potassium opianate prepared from opianic acid (21 grams), potassium carbonate (7 grams), and water (50 c.c.). Silver opianate quickly crystallizes and, when cold, the crystals are collected and washed with alcohol and ether. The silver salt is then treated, during half an hour, in boiling ether (100 c.c.) with methyl iodide (30 grams), the solution filtered, and the silver iodide well washed with ether. The ethereal solution yields, on evaporation, pure methyl opianate. In carrying out the condensation, methyl opianate (11 grams), hippuric acid (10 grams), and fused sodium acetate (4 grams) were mixed with acetic anhydride (25 grams), and heated on the steam-bath during three hours. The red solution so obtained was poured into water, and, after all the acetic anhydride had been decomposed, the solid was collected and drained on porous porcelain in order to remove a trace of oily impurity. The substance crystallizes well from acetic acid in intensely yellow, slender needles, and melts at 134°:

0·1540 gave 0·3700 CO₂ and 0·0670 H₂O. C = 65·5; H = 4·8
 $C_{20}H_{17}O_6N$ requires C = 65·4; H = 4·8 per cent.

This compound is sparingly soluble in alcohol, ether, or ethyl acetate; it dissolves in concentrated sulphuric acid to an orange-red solution.

7:8-Dimethoxyisocarbostyryl-3-carboxylic Acid,

This acid may be obtained from the methyl ester just described by hydrolysis under a variety of conditions, as, for example, by

means of sulphuric acid in acetic acid solution, but it is best prepared and purified in the following manner. The methyl ester (5 grams) is heated on the steam-bath with aqueous potassium hydroxide (50 c.c. of 10 per cent.) during half an hour. Hydrolysis takes place readily, and, at the end of the operation, the clear, red solution is acidified with hydrochloric acid, the precipitate collected and washed well with hot water in order to remove benzoic acid. It is then dissolved in dilute aqueous ammonia, reprecipitated, and finally crystallised from glacial acetic acid, from which it separates in colourless, prismatic needles, melting and decomposing at 261°. Larger crystals of this substance have a brilliant appearance, and sparkle like a diamond. The specimen for analysis was dried at 100°:

0·1206 gave 0·2550 CO₂ and 0·0499 H₂O. C = 57·7; H = 4·6.

0·1898 " 9·2 c.c. N₂ at 15° and 750 mm. N = 5·6.

C₁₂H₁₁O₃N requires C = 57·8; H = 4·4; N = 5·6 per cent.

0·1317 neutralised 0·0216 NaOH, whereas this amount of a monoxime acid, C₁₂H₁₁O₃N, requires 0·0212 NaOH for neutralisation.

Dimethoxyisocarbostyrylcarboxylic acid is very sparingly soluble in the usual organic solvents, but it dissolves to some extent in boiling water, and, on cooling, long slender needles separate. The addition of ferric chloride to the aqueous or alcoholic solution produces a brownish-violet coloration. In contradistinction to its esters, it does not react with benzenediazonium chloride or with nitrous acid.

The *ethyl ester* is readily prepared by boiling the solution of the acid (5 grams) in 5 per cent. alcoholic sulphuric acid (100 c.c.) for three hours. Water is added, the solid collected and crystallised from alcohol, from which the ethyl ester separates in well-defined prisms, melting sharply at 179°:

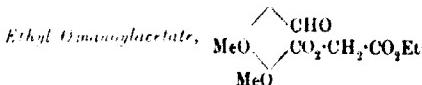
0·1769 gave 0·3875 CO₂ and 0·0852 H₂O. C = 60·5; H = 5·4.

C₁₄H₁₃O₃N requires C = 60·7; H = 5·4 per cent.

The *methyl ester*, prepared in a similar manner, separated from methyl alcohol in groups of slender needles, and melted at 195°. Both esters are sparingly soluble in cold organic solvents, and in their properties exhibit striking differences from those of the parent acid. Their solutions in sulphuric acid are yellow, and give an apple-green fluorescence, whilst ferric chloride develops with their solution or suspension in alcohol, an intense green colour which becomes blue on dilution with water, and this reaction occurs even in the presence of mineral acid.

In faintly alkaline solution or in acid solution in the presence of excess of sodium acetate, both esters yield intense red azo-dyes with diazonium salts, and these dissolve in concentrated sulphuric

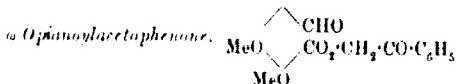
acid with a deep purple colour. On treatment with sodium NO_2 in hot glacial acetic acid solution, the ethyl ester is converted to a yellow, crystalline substance, which melts at 257° . This substance may be a nitroso-derivative, and it is possible that the differences observed between the behaviour of the acid and its ester towards nitrous acid may be due to the lactam configuration of the former and the lactim configuration of the latter, and these configural differences will be made the subject of further investigation.



This ester is obtained when silver opianate (17 grams), suspended in benzene (200 c.c.), is boiled in a reflux apparatus for five hours with ethyl bromoacetate (12 grams). The benzene is then distilled off and the residue dissolved in hot alcohol, when, on cooling, the substance separates in colourless needles, and is obtained pure after one more crystallisation from alcohol:

0.1520 gave 0.3175 CO_2 and 0.0740 H_2O . C = 56.9; H = 5.4.
 $\text{C}_{14}\text{H}_{16}\text{O}_6$ requires C = 56.8; H = 5.4 per cent.

Ethyl opianoylacetate crystallises from alcohol in well-defined prismatic needles, melts at 90° , and is readily soluble in benzene or hot alcohol, but sparingly so in ether. The attempts which have been made to induce this substance to undergo internal condensation have so far been unsuccessful, but further experiments are in progress.

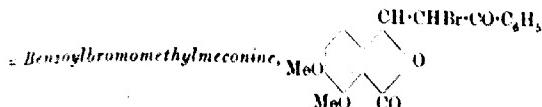


In order to prepare this substance, silver opianate (27 grams) and α -bromoacetophenone (20 grams) were heated during five hours with benzene (250 c.c.) in a reflux apparatus. The solution was filtered, the benzene partly removed by distillation, and dilute alkali was then added, when the ester quickly separated in colourless prismatic crystals, and in almost the theoretical quantity. From analysis, the substance was recrystallised from alcohol:

0.1982 gave 0.4790 CO_2 and 0.0870 H_2O . C = 65.9; H = 4.9.
 $\text{C}_{14}\text{H}_{16}\text{O}_6$ requires C = 65.8; H = 4.9 per cent.

ω Opianoylacetophenone melts at 112° , and is sparingly soluble in cold alcohol or ether, but readily so in boiling alcohol or benzene.

The formation of benzoyldimethoxyisocoumarin from this substance by internal condensation is described on p. 2402.



It is remarkable that this lactone should separate, as it does, on a solution of opionic acid in alcoholic potassium hydroxide is led to an alcoholic solution of ω -bromoacetophenone (compare 2366).

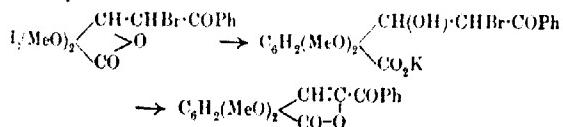
Since, however, the use of alkali hydroxide leads to a partial decomposition of the product, potassium carbonate was employed in its place, and the following conditions were found to work well. A solution of opionic acid (5 grams) in water (20 c.c.) and potassium carbonate (5 grams) was mixed with a solution of ω -bromoacetophenone (5 grams) in alcohol (70 c.c.). The mixture was frequently shaken, and allowed to remain at room temperature during twenty-four hours. Water was then added, the precipitate collected and crystallised from alcohol, from which the substance separated in colourless needles:

M.p. 137 gave 0.2705 CO₂ and 0.0437 H₂O. C 55.2; H 3.6.

M.p. 123 " 0.0712 AgBr. Br 20.3.

C₁₁H₁₁O₂Br requires C 55.2; H 3.8; Br 20.4 per cent.

β-Benzoylthiomameconine melts at 148°, with slight previous tingeing, and is insoluble in alkaline hydroxides in the cold, but dissolves, on boiling, to orange red solutions. On the addition of hydrochloric acid, a sticky, yellow precipitate was formed, which was boiled with a little concentrated hydrochloric acid, washed in water, and dissolved in cold alcohol. The alcoholic solution had deposited a quantity of yellow crystals, which, after recrystallisation from xylene, melted at 171°, and were found to be identical with the benzoyldimethoxyisocoumarin described on p. 2402. The substance was isolated in a similar manner from the solution obtained on boiling opionic acid and ω -bromoacetophenone in alcoholic potassium hydroxide, but in the latter case the yield was very small. The probable course of these interesting changes may be represented thus:

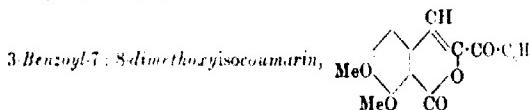




The action of alkaline condensing agents on α -opiatic acetophenone leads, in the first place, to the formation of benzyl dimethoxyisocoumarin (see below), but this substance is readily hydrolysed to the above diketonic acid, and it is therefore the latter which is obtained under the following conditions. α -Opianoyacetophenone (5 grams), pure ether (100 c.c.), and granulated sodium* (1 gram) were heated together in an efficient reflux apparatus, when, in a short time, yellow spangles separate from the solution. After one and a-half hours, alcohol was added to remove the excess of sodium, and then water, and the clear solution was cooled with ice and cautiously acidified with very dilute hydrochloric acid. The yellow precipitate was collected, washed with water until free from every trace of mineral acid, and recrystallised from benzene:

0.1584 gave 0.3899 CO₂ and 0.0720 H₂O. C = 65.6; H = 5.0. C₁₈H₁₆O₆ requires C = 65.9; H = 5.0 per cent.

6-Phenylglyoxylmethyl- α -veratric acid melts rather indefinitely at about 130°, and dissolves in aqueous sodium carbonate to a red solution, from which, if concentrated, the sodium salt separates as red crystals. The fact that the acid and its salts are so highly coloured suggests that both may contain the enolic group -CH=C(OH)-CO-C₆H₅.



The best method for preparing this substance consists in boiling the diketo-acid, just described, with aqueous alcoholic hydrochloric acid for ten minutes. The liquid is diluted with water, the solid collected and recrystallised from alcohol or xylene, from which the substance separates in pale yellow plates:

0.1498 gave 0.3835 CO₂ and 0.0607 H₂O. C = 69.8; H = 4.5. C₁₈H₁₄O₅ requires C = 69.7; H = 4.5 per cent.

Benzoyldimethoxyisocoumarin melts at 171°, is sparingly soluble in most of the ordinary organic solvents, and crystallises with great facility. Some of the yellow spangles which separated will

* Prepared by melting sodium under boiling toluene, shaking vigorously, decanting the toluene and then washing with anhydrous ether.

epianoylacetophenone was boiled with sodium in ethereal solution (p. 2402) were collected, and found to melt at 171°, and at the same temperature, when mixed with the substance obtained from the diketonic acid, as just described; they therefore consisted of benzoyldimethoxyisocoumarin.

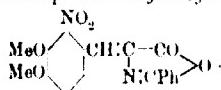
Dibromide.—When benzoyldimethoxyisocoumarin, dissolved in chloroform and cooled to 0°, is gradually mixed with a solution of bromine in chloroform, a bright red precipitate separates in the form of microscopic needles.

This substance would appear to be an oxonium dibromide, since readily loses bromine on exposure to air or on washing with cold chloroform. In a vacuum it also rapidly loses bromine, and pure benzoyldimethoxyisocoumarin remains, and the same change occurs constantly in contact with alcohol. When rapidly heated, the dibromide melts at 113° to a yellow liquid, and, after resolidifying, its melting point is now about 165°. A specimen of the substance as prepared as quickly as possible and analysed at once, but the result, as might be expected, was too low:

0.3328 gave 0.2485 AgBr. Br = 31.8.

$C_{15}H_{14}O_3Br_2$ requires Br = 31.0 per cent.

2-Phenyl-4-o-nitro-mp-dimethoxybenzylideneoxazalone,



In the preparation of this substance, *o*-nitroveratraldehyde (5 grams), hippuric acid (4.3 grams), and fused sodium acetate (2 grams) were mixed with acetic anhydride (10 grams) and heated on the steam-bath for half an hour. The product solidified on cooling, and was collected, washed with water, and crystallised from alcohol, and then from acetic acid, from which it separated in deep yellow, feathery crystals, melting at 145°:

0.1310 gave 0.2926 CO_2 and 0.0480 H_2O . C = 60.9; H = 4.0.

$C_{16}H_{14}O_6N_2$ requires C = 61.0; H = 3.9 per cent.

2-Phenyl-4-o-nitro-p-acetoxy-m-methoxybenzylideneoxazalone, similarly prepared from *o*-nitroacetovanillin, crystallises from alcohol in groups of slender needles, and melts at 167°:

0.1668 gave 0.3668 CO_2 and 0.0560 H_2O . C = 59.9; H = 3.7.

$C_{19}H_{14}O_7N_2$ requires C = 59.6; H = 3.7 per cent.

2-Phenyl-4-o-nitro-mp-methyleneedioxybenzylideneoxazalone, obtained from nitropiperonal and hippuric acid in a similar manner,

2404 SOME DERIVATIVES OF ISOCOUMARIN AND ISOCARBOSTYRIL

crystallises from alcohol in bright yellow needles, and melts at 192°.

0.1996 gave 0.4189 CO₂ and 0.0517 H₂O. C=59.8; H=3.1

C₁₅H₁₄O₂N₂ requires C=60.3; H=2.9 per cent.

2-Nitro-3:4-dimethoxybenzylidenehippuric Acid.—In order to obtain this acid, 2-phenyl-4-*o*-nitro-*mp*-dimethoxybenzylideneoxazolone (10 grams) was heated with 10 per cent. aqueous potassium hydroxide until completely dissolved. The basic solution was then acidified with hydrochloric acid, and the yellow precipitate, which was somewhat oily at first, but soon hardened, was collected and crystallised from ethyl acetate. The acid was thus obtained in slender, greenish yellow needles, and melted at 228°.

0.1350 gave 0.2880 CO₂ and 0.0525 H₂O. C=58.2; H=4.3

C₁₄H₁₃O₂N₂ requires C=58.1; H=4.3 per cent.

When this acid was warmed with acetic anhydride, it at once yielded the oxazolone, melting at 115°.

2-Nitro-3:4-methylenedioxymethylidenehippuric Acid.—2-Phenyl-4-*o*-nitro-*mp*-methylenedioxymethylideneoxazolone, obtained from nitropiperonal in the manner just described, was dissolved in glacial acetic acid, and concentrated hydrochloric acid added in such quantity that the substance only just remained in solution. The mixture was then boiled during ten minutes, cooled, and the crystals which separated collected and crystallised from acetic acid, from which the nitro-acid separates in yellow needles, melting at 215°.

0.2108 gave 0.4120 CO₂ and 0.0634 H₂O. C=57.2; H=3.3

C₁₄H₁₂O₂N₂ requires C=57.3; H=3.3 per cent.

We were not successful in our attempts to hydrolyse this acid further. In an experiment in which the acid was boiled with 10 per cent. alcoholic sulphuric acid, the *ethyl* ester was obtained, and this separates from acetic acid in yellow needles, melts at 17°, and is sparingly soluble in the usual organic solvents:

0.1411 gave 0.3084 CO₂ and 0.0554 H₂O. C=59.4; H=4.3

C₁₉H₁₆O₂N₂ requires C=59.4; H=4.2 per cent.

The authors wish to state that much of the expense of the research was met by grants from the Research Funds of the Royal Society and Chemical Society.

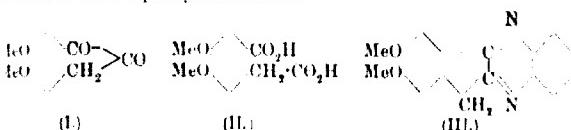
THE UNIVERSITIES OF OXFORD AND SYDNEY.

CCXXIV.—*1:2-Diketo-5:6-dimethoxyhydrindene.*

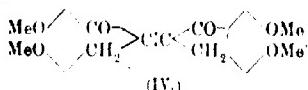
By WILLIAM HENRY PERKIN, jun., WALTER MORELL ROBERTS, and ROBERT ROBINSON.

In a former communication the authors (*T.*, 1912, **101**, 232) have described a convenient method of producing 1:2 diketohydrindene, namely, the hydrolysis of *isom*nitroso 1-hydrindone, by means of formaldehyde and hydrochloric acid. This process has now been applied with even better results to the preparation of 1:2 *diketo-5:6-dimethoxyhydrindene* (I) and of 1:2 *diketo-5:6-methylenehydrindene*, substances which may very probably find an application in solving the difficult problem of the synthesis of azazin and its derivatives.

The properties of the dimethoxy diketone are similar to those of its parent substance; thus the 2-monoxime is produced by reaction with one molecule of hydroxylamine; oxidation with hydrogen peroxide yields 2 carboxy 4:5 dimethoxyphenylacetic acid (II), whilst 5:6-dimethoxyindenquinazoline (III) is formed by condensation with *o*-phenylenediamine:

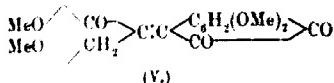


1:2-diketohydrindenes are reactive ketones which enter with ease into various condensations, and we investigated especially the condensation of 1:2-diketo-5:6-dimethoxyhydrindene with 5:6-diethoxy 1-hydrindone, which should produce the indigotin-like dianthrone (IV):



Equimolecular proportions of the components were dissolved in *cet* sufficient acetic acid and warmed on the steam bath with hydrochloric acid (half the volume of the mixture). The condensation product separated, and the liquid became filled with black, microscopic crystals, which were collected. This substance appeared to be a hydrochloride, and was changed to a dark brownish red compound by aqueous sodium acetate. It dissolved in concentrated sulphuric acid to an intense indigo-blue solution. The compound was very sparingly soluble, and separated from pyridine solution as microscopic crystals, but no analysis that was made of it gave

satisfactory figures. Our failure to obtain this compound in a pure condition may be due to its admixture with *anhydrotetra-1,2-diketo-5:6-dimethoxyhydrindene* (V), which was easily obtained by the action of piperidine on 1:2-diketo-5:6-dimethoxyhydrindene (see p. 2408):



EXPERIMENTAL.

1:2 *Diketo-5:6-dimethoxyhydrindene* (I).

iso-Nitroso-5:6-dimethoxy-1-hydrindone (10 grams) (Perkin and Robinson, T., 1907, **91**, 1081) is mixed with formaldehyde (20 c.c. of 40 per cent. aqueous solution) and concentrated hydrochloric acid (5 c.c.), and the liquid heated to incipient boiling while being continually stirred. The *iso-nitroso*-compound passes into complete solution, and almost immediately the diketone begins to separate as a brownish-yellow, crystalline powder. After gently heating during half an hour the mixture is cooled, diluted with water, and the solid collected, washed with water, and dried at 100°. The yield is practically quantitative. The substance is best crystallised from benzene, and is obtained in golden-yellow plates melting at 187°, with previous softening at 160—165°. It is readily soluble in chloroform, but sparingly so in most organic solvents. Unlike 1:2 diketohydrindene, it may be crystallised unchanged from methyl or ethyl alcohols:

0·1271 gave 0·2984 CO₂ and 0·0579 H₂O. C=64·0; H=5·1.
 $\text{C}_{11}\text{H}_{16}\text{O}_4$ requires C=64·1; H=4·9 per cent.

Cold sodium carbonate solution does not affect the substance, but on boiling it is gradually dissolved to a greenish-brown solution from which, if concentrated, a green solid separates, and the unchanged diketone is obtained on acidification. With alkali hydroxide the above reaction is obtained in the cold, whilst, on boiling, the solution which is first green becomes brown and then green again. It is only from the cold solution in potassium hydroxide that the diketone can be regenerated on acidification.

Oxime (iso-Nitroso-5:6-dimethoxy-1-hydrindone).—This derivative is obtained when the diketone is heated with hydroxylamine hydrochloride (1½ mols.) and sodium acetate in alcoholic solution. The crystalline precipitate obtained on cooling the solution was collected and recrystallised from alcohol. The substance melted and decomposed at 235°, and its melting point was not lowered by admixture

with an equal quantity of pure *isonitroso-5:6-dimethoxy-1-hydrindene* (T., 1907, **91**, 1081). From this result we conclude that of the two carbonyl groups in 1:2 diketo-5:6-dimethoxyhydrindene, that in the β -position is the more reactive, and the more likely to enter into all kinds of condensation reactions.

5:6-Dimethoxyindenoquinoxaline (III).

1:2-Diketo-5:6-dimethoxyhydrindene (2·1 grams) and α -phenylenediamine (1·1 grams) were together dissolved in hot ethyl alcohol (5 c.c.). The crystalline product, obtained on cooling the solution, was collected and recrystallised from ethyl alcohol. The slender, yellow needles melt at 177–178°.

On 1196 gave 0·3200 CO₂ and 0·0543 H₂O. C=73·0; H=5·0.

C₁₇H₁₄O₂N₂ requires C=73·4; H=5·0 per cent.

This substance is rather sparingly soluble, and can be crystallised from most solvents. It dissolves in sulphuric acid to a deep violet solution, from which a bright orange sulphate separates on the addition of water, and orange salts are also formed when the quinoxaline is treated with dilute mineral acids. The ferrichloride obtained in the usual way is a brown, microcrystalline powder. The base itself exhibits a strong bluish-violet fluorescence in alcoholic or benzene solution.

Oxidation of 1:2-Diketo-5:6-dimethoxyhydrindene.

In common with other diketones, for example, benzil and phenanthraquinone, this diketohydrindene is readily attacked by hydrogen peroxide, and in this instance the oxidation is readily effected, when the substance is warmed on the steam-bath with dilute alkali and an excess of the reagent, until the yellow colour disappears. The solution was cooled, treated with hydrochloric acid, and the precipitate collected. The substance was crystallised from water, and was found to melt at 215°, and to be completely identical with 2-carboxy-4:5-dimethoxyphenylacetic acid (II), one of the oxidation products of trimethylbrazilin (Perkin, T., 1902, **81**, 1082). The substance obtained by the above oxidation of the diketone when mixed with a specimen which had been obtained by the action of phosphorous pentachloride on *isonitroso-5:6-dimethoxy-1-hydrindene* (Perkin and Robinson, T., 1907, **91**, 1082) melted at 215° (Found, C=55·1; H=5·2. C₁₁H₁₂O₆ requires C=55·0; H=5·0 per cent.).

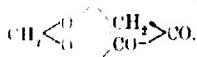
1,4-hydroxy-1,2-diketo-5:6-dimethoxyhydrindene (V).

This condensation product is obtained by boiling 1:2-diketone with dimethoxyhydridene with a few drops of piperidine in alcohol solution or by passing hydrogen chloride into the alcoholic solution. In either case the brownish red product was collected and purified by extraction with boiling alcohol, when a very sparingly soluble red substance remained, which could not be crystallised, although it was distinctly crystalline to the touch and in appearance. Its solution in concentrated sulphuric acid is bright cherry red, and yields a clear yellow liquid on dilution with water.

in 1182 gave 9.2991 CO₂ and 9.0496 H₂O. C=66.9; H=4.7.

$\text{C}_6\text{H}_4\text{O}_2$ requires C = 67.0; H = 4.6 per cent.

1,2-Diketomethylendioxyhydride.



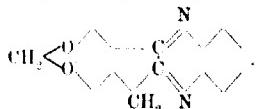
This substance is prepared from *isonitroso-5:6-methylenedioxylhydronone* (Perkin and Robinson, T., 1907, **91**, 1085) by the method already described in the case of the corresponding methoxy compound (p. 2406). It crystallises from benzene as golden yellow needles, which soften at 140° and melt at 166°; the yield obtained was more than 99 per cent. of the theoretical

0.1379 gave 0.3175 CO₂ and 0.0384 H₂O. C, 62.8; H, 3.1.

$\text{C}_6\text{H}_5\text{CO}_2$ requires C = 63.2; H = 3.2 per cent.

This substance is rather less soluble in organic solvents than its corresponding dimethoxy-derivative. Its behaviour with sodium carbonate and potassium hydroxide is similar to that described in the case of 1:2 diketodimethoxyhydrindene. With hydroxy-amine hydrochloride and sodium acetate in alcoholic solution the *B*-monoxime was readily obtained, and melted and decomposed at 230°, either alone or mixed with a specimen of *isonitroso-5:6-methylenedioxy-1-hydrindone* which had been obtained from 5:6 methylenedioxy-1-hydrindone by the action of *isoamyl nitrite* and hydrochloric acid (*loc. cit.*, p. 1085).

5,6-Methylenedioxynindenoquinoroline



When 1:2 diketo-5:6-methylenedioxyhydrindene (2 grams) was heated with *o*-phenylenediamine (1 gram) in alcoholic solution

condensation occurred immediately, and 2·8 grams of the product was obtained on cooling the solution. The quinoxaline crystallises from alcohol in yellow needles melting at 204–205°, and is sparingly soluble in organic solvents in the cold.

at 1255 gave 0·3438 CO₂ and 0·0471 H₂O. C 73·5; H 4·1.

C₁₆H₁₀O₂N₂ requires C 73·3; H 3·8 per cent.

The concentrated alcoholic solution exhibits a green fluorescence, but the dilute solution in benzene shows an intense violet fluorescence. With dilute mineral acids, orange salts are produced, whilst in concentrated sulphuric and hydrochloric acids halochromism is exhibited, the solutions being bluish-violet and reddish violet respectively, and yielding the orange salts on dilution with water. Concentrated ferric chloride acting on the solution of the base in acetic acid and hydrochloric acids produces the *ferrichloride*, which separates as slender, yellow needles.

THE UNIVERSITIES OF OXFORD AND SYDNEY.

CLXXXV.—*The Isomerism of the Oximes. Part V.*
m-Methoxybenzaldoxime, Vanillinoxime, and Veratraldoxime.

By OSCAR LISLE BRADY AND FREDERICK PERCY DUNN.

WHILST ortho- and para methoxybenzaldoximes are well known, the meta-compound does not seem to have been described. In view of their attempts to elucidate the problems connected with the isomerism of the oximes, the authors are of the opinion that it is advantageous to study the variously substituted benzaldoximes as completely as possible, and it is therefore of importance that the effect of the position of each substituent should be considered (compare this vol., p. 821). Additional interest is given to m-methoxybenzaldoxime and its acetyl derivative, since through them the position of the acetyl group in the acetyl derivative of m-hydroxybenzaldoxime may be ascertained (*loc. cit.*).

m-Methoxybenzaldoxime is readily obtained from *m*-methoxybenzaldehyde, and closely resembles the *o*- and *p*-methoxybenzaldoximes. On treatment with acetic anhydride and sodium carbonate solution it yields an acetyl derivative, thereby showing that it possesses the *anti*-configuration. Whilst *p*-methoxybenzaldoxime (anisinaldoxime) is comparatively easy to obtain in the pure state, *o*-methoxybenzaldoxime exists only in the *anti*-form, all

attempts to obtain a second isomeride having so far failed (*loc. cit.*). Although it has not been found possible to isolate *m*-methoxybenzalaldoxime, there is a certain amount of evidence that it exists in the oil obtained on decomposing the hydrochloride of the oxime with sodium carbonate solution. This oil does not crystallise even at low temperatures and after seeding with *m*-methoxybenzalaldoxime, although after keeping for four days it solidifies and then consists entirely of *m*-methoxybenzalaldoxime. Treatment of the oil with acetic anhydride and sodium carbonate solution gives a certain amount of *m*-methoxybenzonitrile, in addition to *anti*-*m*-methoxybenzalaldoxime, the proportions being roughly one to four. This cannot be taken as definitely establishing the presence of the *syn*-compound in the oil, since the *anti*-oxime also yields some nitrile under similar conditions, although in not nearly so large a quantity.

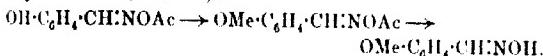
But few disubstituted benzaldehydes have been closely studied, although 3:4-dichlorobenzaldehyde (Erdmann and Schweitzer, *Annalen*, 1890, **260**, 60), piperonaldoxime (Hantzsch, *Zentral. physikal. Chem.*, 1894, **13**, 526), and mesitylaldoxime (Hantzsch and Lucas, *Ber.*, 1895, **28**, 745) have been obtained in two forms. Vanillinoxime and veratraldoxime have been described (Lach, *Ber.* 1883, **16**, 1786; Fulda, *Monatsh.*, 1902, **23**, 913), but the question of the existence of a *syn*-isomeride of these compounds does not seem to have been fully investigated, and the authors have therefore turned their attention to this matter.

Vanillinoxime (4-hydroxy-3-methoxybenzaldehyde) might be expected to resemble *p*-hydroxybenzaldehyde in some respects. The analogy is borne out by the behaviour of this compound with acetic anhydride; treatment with acetic anhydride and sodium carbonate solution yields a diacetyl derivative, thus establishing the *anti* configuration of the oxime, whilst solution in warm acetic anhydride and subsequent evaporation of excess of the reagent in a vacuum gives a monoacetyl derivative (compare Brady and Dunn, *loc. cit.*). Vanillinoxime, however, differs from *p*-hydroxybenzaldehyde in that in the monoacetyl derivative the oximino- and not the phenolic group is acetylated.

Vanillinoxime readily forms a hydrochloride in the usual way but on decomposing this compound with sodium carbonate solution the original *anti*-oxime is obtained, as would be expected from analogy to the hydroxybenzaldehydes (Brady and Dunn, *loc. cit.*). The hydrochloride of veratraldoxime behaves similarly to that of *m*-methoxybenzalaldoxime. On decomposing with sodium carbonate solution an oil is first formed which, on being scratched, soon sets to a solid melting at about 56°; the *anti*-oxime melts at 94–95°.

Treatment of this substance of low melting point with acetic anhydride and sodium carbonate solution yields a mixture of *3:4-dimethoxybenzonitrile* (veratronitrile) and acetyl *3:4-dimethoxybenzaldoxime* (acetylveratraldoxime), the latter, however, greatly predominating. Under similar conditions the *anti*-oxime also yields a small quantity of the nitrile with the acetyl derivative. After twelve hours the melting point was found to have risen from 62° to 88°, and on recrystallisation all fractions consisted of the *meta*-oxime. This result was always obtained; it may be that the rise in melting point is merely due to the substance becoming free from moisture, but it is possible that the low melting point is due to the presence of a small quantity of the *syn*-isomeride, which is unstable.

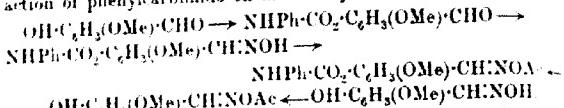
The position of the acetyl group in the acetyl derivative of *m*-hydroxybenzaldoxime and in the monoacetyl derivative of vanillinoxime has also been investigated. In the first case the acetyl derivative of *m*-hydroxybenzaldoxime was methylated with ethyl iodide and dry silver oxide in dry ethereal solution. It was not, however, possible to show that the substance so obtained was identical with the acetyl derivative of *m*-methoxybenzaldoxime as obtained from *m*-methoxybenzaldehyde and acetic anhydride, as the product in each case was an uncrySTALLISABLE oil. Their boiling points could not be determined, as these compounds decompose on boiling under the ordinary pressure. On hydrolysis of the methylation product, however, *m*-methoxybenzaldoxime was obtained, thus establishing that, as in the case of the ortho- and *p*-distinction from the para-compound, the acetyl derivative of *m*-hydroxybenzaldoxime has the oximino-group acetylated (compare Brady and Dunn, *loc. cit.*):



The possibility that the phenolic group was acetylated, and that under the conditions of the experiment the acetyl group was removed and the methyl group substituted is obviated by the fact that the oximino-group would also have been methylated, as *m*-methoxybenzaldoxime readily yields the *O*-methyl ether (*m*, *p*, 3) under similar conditions. Since by acting on *m*-hydroxybenzaldoxime with acetic anhydride followed by sodium carbonation the oximino-group is acetylated and *m*-hydroxybenzonitrile is not produced, it follows that this oxime possesses the *anti*-configuration.

With the monoacetyl derivative of vanillinoxime the task proved more difficult, as the method employed above failed to yield a crystalline product; a second method of solving the question sug-

gented itself, namely, to obtain the carbanilino-derivative of vanillin by acting on vanillin with phenylcarbamide, preparing the oxime from this, and acetylating. Then if in the acetyl derivative of vanillinoxime the oximino-group is acetylated, it follows that the compound obtained would be identical with the product of the action of phenylcarbamide on monoacetylvanillinoxime:



This method, however, proved unsuccessful, as on treating *m*-aminovanillin with hydroxylamine hydrolysis occurred even at the cold with the production of diphenylcarbamide and vanillinoxime. This was unexpected, as the authors have found that the carbamino-derivatives of the hydroxybenzaldehydes can be oximated without special precautions. These compounds will form the subject of a subsequent communication.

Another method of attacking the problem was the preparation of acetovanillinoxime, $\text{OAc-C}_6\text{H}_3(\text{OMe})\text{-CH:NOH}$, by oximating *m*-acetovanillin, and showing that this compound is either different from or the same as the acetyl derivative of vanillinoxime.

An uncrySTALLISABLE oil was obtained by this method, but this is, however, considerable evidence to show that the substance obtained was acetovanillinoxime, namely, its hydrolysis by alkali to acetic acid and vanillinoxime, and the formation of a hydrogen chloride in the usual way which regenerated the oil on treatment with sodium carbonate solution. As this compound is not similar to the acetylvanillinoxime obtained by the acetylation of the oxime, it would appear that in the latter compound it is the oximino group that is acetylated. Moreover, the analogous behaviour of *m*-acetylvanillinoxime and acetylsalicylaldoxime on treatment with hydrogen chloride in ethereal solution confirms this conclusion (see experimental part).

EXPERIMENTAL.

m-Methoxybenzalaldoxime.

m-Methoxybenzaldehyde was dissolved in alcohol, and to it were added $1\frac{1}{2}$ equivalents of hydroxylamine hydrochloride and 2 equivalents of sodium hydroxide, each dissolved in a small quantity of water. The mixture was left for twenty-four hours, then diluted with water, and the oil which separated was extracted with ether. After removing the ether, the oil was left overnight on ice, where it solidified to a crystalline mass. This was pressed on a glass plate, and recrystallised from benzene and light petroleum.

m-Methoxybenzaldoxime forms colourless crystals, melting at -40° :

$\text{C}_{11}\text{H}_9\text{O}_2$ gave 0.2678 CO₂ and 0.0634 H₂O. C = 63.3; H = 6.1.

$\text{C}_{11}\text{H}_9\text{O}_2$, 0.5244 AgI. OMe = 20.9.

$\text{C}_8\text{H}_9\text{O}_2\text{N}$ requires C = 63.5; H = 5.9; OMe = 20.5 per cent.

Acetyl-m-methoxybenzaldoxime.—The oxime was dissolved in moderate excess of warm acetic anhydride and left for three days in a vacuum over concentrated sulphuric acid and calcium pyrooxide. At the end of that time the liquid no longer had the colour of acetic anhydride, but did not solidify even at -25° . As the acetyl derivatives of the oximes are often decomposed on distillation, a portion of the liquid was left over potassium hydroxide for several weeks, and the acetyl group determined in this specimen by A. G. Perkin's method:

$\text{C}_{11}\text{H}_9\text{O}_2$ required 6.1 c.c. N/2-KOH. Ac = 21.7.

$\text{C}_{11}\text{H}_9\text{O}_2\text{N}$ requires Ac = 22.2 per cent.

m-Methoxybenzsynaldoxime.

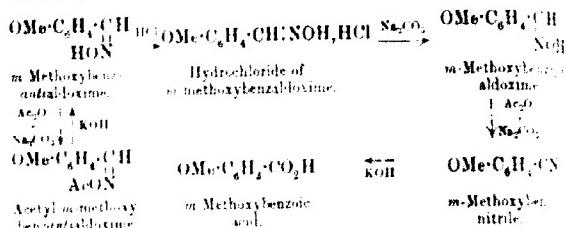
m-Methoxybenzaldoxime was dissolved in dry ether, and the solution saturated with dry hydrogen chloride. A copious, white precipitate was obtained, which was dried on a porous plate. This hydrochloride melts at 110–112°. A chlorine determination was made by decomposing the hydrochloride with sodium hydroxide, boiling with nitric acid, and estimating the chlorine volumetrically.

$\text{C}_{11}\text{H}_9\text{O}_2$ required 15.7 c.c. N/10-AgNO₃. Cl = 18.4.

$\text{C}_8\text{H}_9\text{O}_2\text{N}, \text{HCl}$ requires Cl = 18.8 per cent.

On decomposing the hydrochloride with sodium carbonate solution, extracting the oil so formed with ether, and then removing the ether with a current of air, an uncrystallisable oil was obtained, which did not solidify in a freezing mixture. A portion, kept in a separator over potassium hydroxide for four days, on cooling in a set to a solid mass of *m*-methoxybenzaldoxime. Another portion was at once treated with acetic anhydride, and the reaction mixture decomposed with sodium carbonate solution. This treatment converts *syn*-oxime into nitrile and *anti*-oxime into the *anti*-acetyl derivative. As both these compounds are oils and the acetyl derivative would readily decompose on distillation, giving the nitrile, it was impossible to separate them. The mixture was therefore boiled with a solution of potassium hydroxide under reflux for thirty minutes; there was a copious evolution of ammonia, indicating the presence of nitrile, and the oil dissolved completely. The solution, which contained the sodium salt of the *anti*-oxime and

of *m*-methoxybenzoic acid (obtained from the nitrile), was acidified, made alkaline with sodium carbonate, and extracted with ether. In this way the oxime was removed and recovered from the ether extract. The aqueous solution was acidified, and the *m*-methoxybenzoic acid extracted with ether. It was found that a little less than 1 gram of the acid was obtained and 4 grams of the oxime. It seems, therefore, that about one-fifth of the acetylation product consists of *m*-methoxybenzonitrile. That so large a quantity is formed seems to indicate the presence of a certain amount of *cis*-cyclooxime in the original oil. This would account for the difficulty crystallising when first prepared. The course of the reaction described above is as follows:



Luxmore (T., 1896, **69**, 179) has shown that the hydrochloride of benzalloxime (m. p. 103–105°), which regenerates the oxime on treatment with ammonia and ice, is converted, on crystallisation, into the hydrochloride (m. p. 66–67°), which yields *cis*-oxime on similar treatment. Hence it was thought advisable to try the effect of recrystallising the above hydrochloride, since formation of the mixture of the *anti*- and *syn* oximes might be due to the precipitation of two hydrochlorides. Recrystallisation, however, of the hydrochloride from chloroform and light petroleum did not affect its melting point or other properties.

Action of Hydrogen Chloride on Vanillinoxime.

The vanillinoxime was prepared in the usual way, and recrystallised from benzene and light petroleum. The compound was dissolved in dry ether, and the solution saturated with dry hydrogen chloride, when a pale yellow hydrochloride, melting at 139°, was precipitated:

0.3176 required 1.65 c.c. $N/10\text{-AgNO}_3$. Cl = 17.3.

$\text{C}_8\text{H}_8\text{O}_2\text{N.HCl}$ requires Cl = 17.4 per cent.

When this compound was decomposed with sodium carbonat^e solution, a small quantity of solid remained, which proved to be vanillinoxime (m. p. 117°); the greater part of the oxime, howev-

is dissolved, and was extracted with ether, and after removal of the ether the product was found to be the original vanillinoxime.

Monoacetylvanillinoxime.

Vanillinoxime was dissolved in excess of cold acetic anhydride, and the solution left for some weeks over concentrated sulphuric acid and calcium hydroxide in a vacuum. At the end of that time most of the excess of acetic anhydride had volatilised, and the acetyl derivative had separated in nodules of needle-shaped crystals. These were pressed on a porous plate and recrystallised from dilute alcohol, when colourless needles melting at 114° were obtained:

— 142 gave 0·2188 CO₂ and 0·0498 H₂O. C = 57·3; H = 5·3.
— 140 " 14·6 c.c. N₂ at 26° and 757 mm. N = 6·9.
— 267 " 0·2320 AgI. OMe = 14·8.
 $C_8H_{11}O_4N$ requires C = 57·4; H = 5·2; N = 6·7; OMe = 14·8 per cent.

The action of dry hydrogen chloride on this compound in dry ether resembles that of this reagent on the acetyl derivative of acylaldoxime (compare Brady and Dunn, *loc. cit.*). At first no visible change takes place, but after some ten minutes the liquid gradually becomes deep red. No hydrochloride is, however, obtained, but, after some time, a small quantity of a dark red compound is precipitated, the yield, however, being too small to admit of investigation. The similarity of the behaviour of monoacetylvanillinoxime in this respect to acetylsalicylaldoxime suggests that the acetyl group occupies the same position in these compounds, that is, the oximino- and not the phenolic group is acetylated. In the case of the monoacetyl derivative of *p*-hydroxybenzaldehyde the reverse is the case, and a hydrochloride of *p*-acetoxybenzaldehyde is precipitated on treatment of an ethereal solution with dry hydrogen chloride (compare Brady and Dunn, *loc. cit.*). It has not been found possible so far to determine the conditions under which the di-compound described above is formed, or to prepare any quantity of it, and the authors are not able to offer any suggestion as to its formation.

Diacetylvanillinoxime.

Vanillinoxime was dissolved in warm acetic anhydride, and the solution allowed to remain for ten minutes, when it was shaken with sodium carbonate solution until it no longer possessed the taste of acetic anhydride. The solid which had separated was collected, washed, and recrystallised from dilute alcohol, when it separated in very pale rose-pink needles melting at 95°:

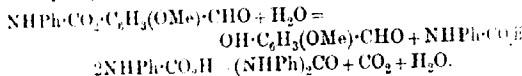
0.1326 gave 0.2772 CO₂ and 0.0694 H₂O. C=57.0; H=5.9.
 0.3139 " 16.6 c.c. N₂ at 26° and 756 mm. N=5.5.
 0.3619 " 0.3409 AgI. OMe=12.4.
 $C_{12}H_{13}O_3N$ requires C=57.3; H=5.1; N=5.5; OMe=12.3 per cent.

Carbanilinovanillin, C₆H₅·NH·CO₂·C₆H₅(OMe)·CHO

Vanillin was dissolved in dry ether in a stoppered bottle, a small molecular amount of phenylcarbimide added. The bottle was tightly stoppered and left for twenty-four hours. At the end of that time the greater portion of the carbanilino-derivative had crystallised out in bunches of fine needles, which were collected, pressed on a porous plate, and recrystallised from alcohol. A further quantity was obtained by evaporating the ethereal solution in a current of dry air. *Carbanilinovanillin* crystallises in very fine needles melting at 116--117°:

0.3590 gave 17.0 c.c. N₂ at 24° and 750 mm. N=5.4.
 $C_{13}H_{13}O_4N$ requires N=5.2 per cent.

In attempting to prepare the oxime this compound was dissolved in alcohol and hydroxylamine hydrochloride (1.5 mols.), and solid sodium hydroxide (1 mol., insufficient to decompose all the hydroxylamine hydrochloride in order to avoid free sodium hydroxide in the solution) were added, each being dissolved in a little water. The mixture was left for twenty-four hours in the ice-chest. The red product was diluted, and the small quantity of solid mass which separated was collected. On crystallisation this solid gave diphenylcarbamide (m. p. 232°), a product of hydrolysis:



The aqueous alcoholic solution was extracted with ether, and ether evaporated, but from the dark-coloured solid so obtained vanillinoxime and diphenylcarbamide could be obtained by hydrolysis of the carbanilino-aldehyde under these conditions, therefore, to be practically complete.

Action of Hydrogen Chloride on Veratraldoxime

Veratraldoxime was obtained in the usual way from veratraldehyde, and was treated in dry ethereal solution with dry hydrogen chloride. A pale pink *hydrochloride* was precipitated, which at 151°:

0.2854 required 13.0 c.c. N/10-AgNO₃. Cl=16.1.
 $\bullet\text{C}_9\text{H}_{11}\text{O}_3\text{N},\text{HCl}$ requires Cl=16.3 per cent.

This hydrochloride on decomposition with ice-cold sodium carbonate solution gives an oil which slowly solidifies on scratching. This melts at about 56°, but after recrystallising from cold benzene or light petroleum it melts at 88°, and does not sensibly depress the melting point of veratraldoxime (m. p. 94°). Small quantities kept in a desiccator and in the open air for twenty-four hours, in each case the melting point rose to above 84°, and the substance seemed to be almost pure veratraldoxime. Treatment of a substance of low melting point with acetic anhydride, and subsequently sodium carbonate solution, gave a small quantity of triole, but mainly the acetyl derivative of veratraldoxime, as shown by hydrolysis of the acetylation product with potassium dioxide, ammonia, a very small quantity of dimethoxybenzoic acid, and veratraldoxime being the products.

Attempts were made to prepare a *syn*-oxime from veratraldoxime by slightly different methods. Chloroform was substituted for ether in the preparation of the hydrochloride, but the latter was found to be soluble in this solvent, and was precipitated on the addition of ether. The hydrochloride so obtained proved to be identical with that described above.

The hydrochloride was fractionally crystallised from chloroform and ether in the hope of separating it into two substances (see above), but without success. It was also decomposed by adding to an ice cold solution of sodium carbonate, on which was floating a layer of benzene, thus ensuring the rapid removal from the sodium carbonate solution of the oxime as formed. The benzene layer was separated, dried, and light petroleum added; the compound precipitated proved, however, to be the original *anti*-oxime.

Acetylveratraldoxime.

Veratraldoxime was acetylated in the usual way by treatment with acetic anhydride and subsequently with sodium carbonate solution to remove excess of the anhydride. The acetyl derivative did not solidify, so the oil was extracted with ether; after removal of the ether the oil, on being cooled in a freezing mixture and then scratched, set to a solid, which was pressed on a porous plate and recrystallised from light petroleum. It forms colourless crystals melting at 68°.

0.1972 gave 0.2318 CO₂ and 0.0569 H₂O. C = 58.9; H = 5.9.

C₁₁H₁₃O₄N requires C = 59.2; H = 5.8 per cent.

O-Methyl Ether of Veratraldoxime.

To a solution of veratraldoxime in alcohol an equivalent amount of sodium dissolved in alcohol was added, followed by a slight excess

of methyl iodide. The mixture was heated for ten minutes on the water bath, diluted, and extracted with ether. The ethereal solution was shaken first with dilute sodium hydroxide solution, and then with water to remove unchanged oxime; the ether was removed, and the oily product distilled in a current of steam. $\text{I}.$ *O*-methyl ether distilled in oily drops, which soon solidified in the receiver. The solid was recrystallised from dilute alcohol, when it formed colourless needles melting at $59-60^\circ$, having a sharp but rather unpleasant odour, differing in this respect from the other *O*-ethers of the oximes, which have a pronounced and fragrant smell.

0.3684 gave 23.7 c.c. N_2 at 25° and 756 mm. $\text{N} = 7.3$.

0.3429 " 22.1 c.c. N_2 at 25° and 756 mm. $\text{N} = 7.4$.

$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{N} = 7.2$ per cent.

It is noteworthy that this is another of those compounds containing several methoxyl groups which, owing to the formation of methane, give abnormal results by Dumas' method for determining nitrogen. Correct analyses can be obtained, however, if the substance is mixed with cuprous chloride before introduction into the tube.

*Determination of the Position of the Acetyl Group in Acetyl-*m*-methoxybenzaldoxime and in Monoacetylvanillinoxime.*

Acetyl *m*-hydroxybenzaldoxime was dissolved in dry ether, excess of dry silver oxide and methyl iodide added. After standing and leaving for some days the solution was filtered, and the ether and excess of methyl iodide were removed. The colourless uncrystallisable oil was boiled for three minutes with 2*N* sodium hydroxide, the mixture acidified and extracted with ether. On removing the ether an oil was obtained, which solidified in a cooling mixture, and proved to be *m*-methoxybenzaldoxime, having a melting point and comparison with that substance.

The monoacetyl derivative of vanillinoxime was treated in the same way, but as no crystalline compound could be obtained, the method was abandoned, and an attempt to solve the problem was made through the preparation of acetovanillinoxime, a compound in which the acetyl group is undoubtedly attached to the phenolic hydroxyl group. Acetovanillin, prepared by Pschorr and Schleunig's method (*Ber.*, 1899, **32**, 3407), was oxidated by dissolving it in alcohol and adding hydroxylamine hydrochloride (1.5 mol.) and sodium hydroxide (1 mol.), each dissolved in a little water, the mixture being cooled during the addition. The mixture was left for twenty-four hours in the ice-chest, and was then diluted.

ed, and extracted with ether. After removing the ether an oil was obtained, which did not crystallise even when cooled to -25°. This oil was left for some weeks in an exhausted desiccator over potassium hydroxide, but did not solidify; it was too readily soluble to be crystallised from diluted alcohol or acetone, good solvents for the recrystallisation of monoacetylvanillinoxime, and it separated as an oil from benzene and light petroleum. Attempts to crystallise this substance by means of the preparation of the hydrochloride were also unsuccessful. Dry hydrogen chloride, when assayed into a dry ethereal solution of the oil, precipitated a viscid hydrochloride, which on treatment with sodium carbonate solution yielded an uncrySTALLISABLE oil (compare Brady and Dunn, *loc. cit.*). The compound on hydrolysis with 2*N* potassium hydroxide yields acetic acid and vanillinoxime; on exposure to moist air decomposition slowly takes place, acetic acid being formed and vanillin oxide crystallising out. The oil appears to consist mainly of tetravanillinoxime, $\text{AcO-C}_6\text{H}_3(\text{OMe})\text{CH}_2\text{NOH}$, and consequently the crystalline monoacetylvanillinoxime previously described must have the structure $\text{HO-C}_6\text{H}_3(\text{OMe})\text{CH}_2\text{NOAc}$.

In conclusion, the authors wish to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of this research.

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THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.

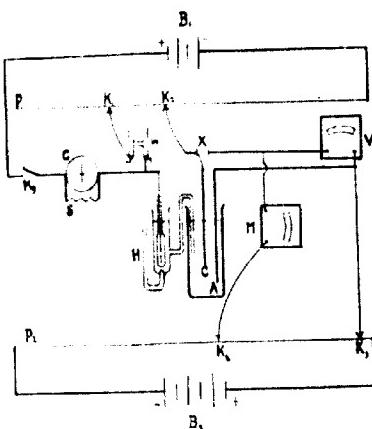
CXXVI.—*Overtoltage*.

By EDGAR NEWBERY.

The whole subject of overvoltage, its properties, magnitude, and determining factors, is at present in such an undecided state, in spite of extensive researches already carried out, that the following work was originally begun mainly with the idea of helping to decide between the many different theories put forward. In the course of the investigation, however, a number of new phenomena were observed for which no existing theory can account. The final explanation offered, therefore, embraces some of the principles set forward in the earlier theories, together with new determining factors which have been established for the first time in this work. A precise statement of what is understood by the term "overvoltage" in this paper is first necessary, as different authors have used the term in slightly different senses.

If an oxygen and a hydrogen electrode in dilute sulphuric acid be combined to form an electrolytic cell, the potential of the cell will be about 1.1 volt. If, now, an *E.M.F.* of 1.1 volt be applied from an external source in opposition to the cell, the back *E.M.F.* set up by the latter will neutralise the applied potential, and no current will flow. If the applied potential be now increased, the back *E.M.F.* will also increase up to a certain limit, and until this limit is exceeded by the applied potential, no permanent current will flow. This increase of the back *E.M.F.* above the normal is the overvoltage of the cell as a whole, the increase of potential at each electrode being termed the anodic and cathodic overvoltage respectively.

FIG. 1.



Throughout this paper, cathodic overvoltage is to be understood unless the contrary is stated.

Apparatus. A long series of preliminary experiments was first carried out before it was found possible to suppress the great number of disturbing factors encountered when measuring overvoltage.

The form of apparatus finally found to be the most accurate is shown in Fig. 1.

The variable, applied *E.M.F.*, was taken from the movable pads K_2 , K_4 on the potentiometer P_2 , the current passing along the path $A'C'AM$. The current density was determined by means of the milliammeter M , and the voltage, when required, by the voltmeter V . The commutator X , rotating 2500 times a minute,

ternately made this circuit and broke it, at the same time connecting the cathode C in a circuit containing an accurately calibrated metre bridge P_1 , a galvanometer G , and a standard hydrogen electrode H . The galvanometer was a very sensitive Mather reflecting instrument, and an adjustable shunt S was attached to vary the sensitiveness when required.

A Weston cadmium cell W ($E.M.F. = 1.0185$ volt) was used as standard of $E.M.F.$.

When hydrogen was being liberated from C , if overvoltage were sent, the potential of C should be the same as that of the hydrogen electrode H . The actual difference observed and measured on the potentiometer P_1 therefore gave at once the static overvoltage of the metal C .

Scope of Experiments.—The following determinations were made in this series:

- (1) The overvoltage, as far as possible under normal conditions, of a number of different metals.
- (2) The influence of current density and time, including the effect of breaking the circuit for definite intervals.
- (3) The influence of colloids.
- (4) The production of physical changes in the surface as revealed by microscopic examination.
- (5) The influence of high gaseous pressures.
- (6) Measurement of the ionisation of the gas liberated.

(1a) *Overtension of Lead.*—A small rod of pure electrolytic lead was made by casting in a glass tube, and was partly covered with hard sealing-wax, leaving only 1 sq. cm. exposed. This was the cathode in the apparatus just described, the anode being a large platinised platinum plate.

The solution used was 10 per cent. sulphuric acid in carefully distilled conductivity water.

Current densities of 100, 200, and 300 milliamperes per sq. cm. were used, as it was found that for most metals the change of overvoltage with current density is small over this range.

The average of about seventy measurements * is given below:

Current density.....	100	200	300	mill. amps. per sq. cm.
Overvoltage	0.66	0.65	0.64	volt

Maximum deviation from the average ± 0.05 volt.

A measurement of the direct difference of potential between C and H (Fig. 1) was also made while the current was passing by

* Measurements given in this section were obtained by alternately increasing and decreasing the current density between 100 and 300 milliamperes per sq. cm., about ten minutes being required for each reading. After this had been continued for about fifteen minutes the current was interrupted, the metal examined and cleaned thoroughly, and the whole process repeated.

simply short-circuiting the commutator X . Under these conditions, the increased potential at the cathode necessary to overcome the resistance of a film of gas round it is measured in addition to the true overvoltage or back *E.M.F.*

The average of about forty measurements is as follows:

Current density	100	200	300 mil. amps. per sq. cm.
Direct potential difference ...	1.16	1.32	1.44 volt.

Maximum deviation from the average ± 0.20 volt.

(1b) *Overtvoltage of Platinum.*—Experimental details were the same as with lead.

Current density	100	200	300 mil. amps. per sq. cm.
Overtvoltage	0.97	0.98	0.98 volt.

Maximum deviation from the average ± 0.015 volt.

The same with commutator short-circuited:

Current density	100	200	300 mil. amps. per sq. cm.
Direct potential difference ...	0.36	0.65	0.88 volt.

Maximum deviation from the average ± 0.20 volt.

The direction of the current in the experimental cell was reversed, the small platinum plate being now the anode:

Current density	100	200	300 mil. amps. per sq. cm.
Anodic overvoltage	0.56	0.56	0.56 volt.

Maximum deviation from the average ± 0.01 volt.

(1c) *Overtvoltage of Mercury.*—A small glass cup 1 sq. cm. cross section, sealed on to a U tube containing mercury, was used as cathode, connexion with the rest of the apparatus being made by means of a platinum wire dipping in the mercury.

In this case there appear to be two series of values for the overvoltage which coincide at very high and very low current densities, but are widely divergent with moderate current densities. The results are shown in tabular form in Section 2.

(1d) *Overtvoltage of Zinc.*—In this case, the method was modified in order to obtain the overvoltage when the metal is being deposited instead of hydrogen.

The solution used throughout the apparatus, including the hydrogen electrode, was 10 per cent. sulphuric acid, as before; the experimental vessel contained also sufficient zinc sulphate to make the liquid of 10 per cent. strength in zinc.

To obtain a true measure of the overvoltage here, where zinc is being liberated, a standard zinc electrode should be used instead of the hydrogen electrode. Since the hydrogen electrode was chosen as being more convenient, and the difference in potential between this and a zinc electrode is 0.770 volt, the measured values of the overvoltage of zinc should all be reduced by 0.77 volt.

This has been done in the following tables:

Current density 100 200 300 mil. amps. per sq. cm.
 $E_{\text{overvoltage}}$ 0.081 0.092 0.094 volt.

Maximum deviation from average = ± 0.004 volt.

The same with commutator short-circuited:

Current density 100 200 300 mil. amps. per sq. cm.
 Direct potential difference ... 0.28 0.44 0.56 volt.

Maximum deviation from average = ± 0.025 volt.

2. The Influence of Current Density and Time. The influence of these two factors is so great and so confusing that the figures given in Section 1 (with exceptions, to be referred to later) must be taken rather as typical of those which may be obtained than as accurately reproducible data.

The following table shows the variation of the overvoltage of lead with change of current density:

Current, Mil. amperes	Over- voltage, Volt.	Current, Mil. amperes	Over- voltage, Volt.	Current, Mil. amperes	Over- voltage, Volt.
10	0.62	50	0.70	90	0.67
20	0.64	60	0.68	100	0.67
30	0.66	70	0.67	200	0.66
40	0.71	80	0.67	300	0.64

The readings in this and in the following table were taken at intervals of about two minutes, so that the influence of time would not cases be comparable.

The following table shows the variation in overvoltage with current density of platinum, mercury, and zinc, that of platinum and mercury being measured during liberation of hydrogen, and of zinc during deposition of the metal.

Two series are given for mercury. These were obtained with the same mercury at different times, and well illustrate the erratic behaviour of mercury under these conditions.

Current density per sq. cm. Mil.amperes	Platinum		Mercury		
	Cathodic, Volt.	Anodic, Volt.	Series 1, Volt.	Series 2, Volt.	Zinc, Volt.
10	0.06	0.56	0.74	0.54	0.089
20	0.08	0.56	0.70	0.45	0.089
50	0.06	0.56	0.67	0.40	0.090
100	0.07	0.56	0.64	0.30	0.091
200	0.08	0.56	0.59	0.07	0.092
300	0.08	0.55	0.54	0.08	0.094
500	0.05	0.55	0.16	0.04	0.094
1000	0.03	0.55	- 0.01	0.01	0.095
2000	- 0.03	0.54	0.05	0.05	0.096

In these tables it should be noted that platinum and lead show a preliminary rise and then a fall of cathodic overvoltage as the

current density increases; platinum shows a very slight fall of anodic overvoltage, mercury a very large fall of cathodic overvoltage, and zinc a very small rise throughout. A discussion of the reasons for these changes will be made later.

Influence of Time.—In the complicated relation between the magnitude of the cathodic overvoltage and the duration of electrolysis the following observations were made:

Platinum.—Current density, 300 mil. amps.; 400 mil. amps. per sq. cm.:

	Volt.	Volt.
Overtoltage after 1 minute.....	0.076	0.060
" 5 "	0.080	0.065
" 15 "	0.088	0.092
" 30 "	0.100	0.104
" 1 hour "	0.112	0.120
" 6 "	0.173	0.236
" 12 "	0.401	0.200
" 24 "	0.511	0.120
After 5 minutes rest with no current.....	0.080	
" further ten minutes with current ...	0.122	

Mercury.—Current density, 20 mil. amps. per sq. cm. Overvoltage measured at intervals of three minutes: 0.24, 0.32, 0.35, 0.50, 0.54, 0.62, 0.66, 0.69, 0.76, 0.75, 0.77, 0.76 volt.

Current density, 60 mil. amps. per sq. cm. Overvoltage measured at intervals of three minutes: 0.44, 0.43, 0.42, 0.41, 0.33, 0.30, 0.32 volt.

Zinc (metal being deposited).—Current density, 100 mil. amp. per sq. cm. Overvoltage measured at intervals of ten minutes: 0.094, 0.092, 0.091, 0.091, 0.091 volt.

The general conclusions arrived at are as follows. When hydrogen is being liberated with a low current density, the overvoltage increases with time, apparently without limit in the case of platinum, and to a high but variable limit in the case of mercury.

With a high current density, the overvoltage of lead, platinum, and mercury at first increases, reaches a maximum in the position which depends on the current density, and then falls slowly. The time taken to reach the maximum is very small in the case of mercury and lead, and great in the case of platinum, but is diminished in all cases by increase of current density. When a metal is being deposited, the time effect is almost negligible, only a very slight fall of overvoltage being observed with high or low current densities.

The effect of breaking the circuit for a definite interval has been mentioned in this section in the case of platinum. The same experiment tried with lead gave a similar result. On re-making the circuit, the overvoltage was found to be much less

than before, but rapidly rose to a very high value, afterwards falling slowly.

With mercury at low current densities, a slight lowering of the overvoltage was caused by similar treatment, due, probably, to a diffusion of hydrogen from the surface deeper into the metal. On re-making the circuit, the overvoltage soon rose to its former value, but not above it, as with lead and platinum.

At high current densities, the effect of breaking circuit on mercury was exactly reversed, the overvoltage being first raised and then lowered by the treatment. Zinc, when metal was being dissolved, showed none of these effects.

(3) *The Influence of Colloids.* It has been found by Le Blanc ("Die Elek. Kräfte der Polarisation," Knapp, Halle, 1910) and by Pring and Tainton (this vol., p. 710) that colloids exert a very large influence on the electrolysis of solutions of metallic salts. This influence has been attributed to a number of causes, which also operate in the determination of overvoltage. It therefore became of importance in the present investigation to make comparative measurements of the effect of several colloids on overvoltage.

(4) *Influence on Overvoltage of Lead.* The following table gives the average values for the overvoltage of lead in 10 per cent. sulphuric acid containing various colloids, current densities from 20 to 300 milliamperes per sq. cm. being employed:

Without colloid, overvoltage	0.65 volt
With 0.05 per cent. of dextrin, overvoltage	0.63 ..
" 1.0 " " "	0.75 ..
" 0.02 " " gelatin	0.75 ..
" 1.0 " " "	0.80 ..

The following points were observed when making these measurements:

(i) The time effect referred to in the preceding section is greatly altered. The time required to reach a maximum overvoltage with a given current density was increased thirty- to sixty-fold by the presence of 0.02 per cent. gelatin, and when 1 per cent. gelatin was present no maximum could be attained in twenty-four hours.

(ii) The current-density effect is also greatly altered. At low current densities the overvoltage was only slightly changed, but at high current densities the fall of overvoltage with increasing current was practically eliminated by the presence of 1 per cent. gelatin.

(iii) When first placed in a solution containing a colloid, the metal showed an overvoltage little different from that in pure acid with moderate current densities, but this soon rose to the value even above.

If, now, this metal was taken out, washed with distilled water, and even lightly scraped with a razor blade, and its overvoltage then measured in pure acid, the value at first given corresponded with that in the solution containing a colloid, and only slowly returned to its normal value for pure acid. Heavy scraping with the razor blade at once restored the normal value.

This fact furnishes strong evidence for the supposition that the colloid penetrates the metal surface before affecting the overvoltage.

(b) and (c) Influence on Overvoltage of Platinum and Mercury.

The effect of the presence of colloid in these two cases was very much the same as with lead.

At low current densities the overvoltage was raised very slightly, whilst at high current densities the overvoltage remained nearly constant. This is illustrated by the following table, which refers to platinum in a solution containing 0·05 per cent. of gelatin. The values of the overvoltage without colloid are added for the sake of comparison:

Current density per sq. cm.	Overvoltage	
	With colloid.	Without colloid.
20 milliamperes	0·08	0·06
50 "	0·09	0·06
100 "	0·10	0·07
200 "	0·10	0·08
500 "	0·10	0·05
1000 "	0·10	0·03
2000 "	0·09	0·03

(d) Influence on Overvoltage of Zinc.—The effects in this case were studied in greater detail in order to determine whether the remarkable influence exerted by colloids on the nature of the deposit when a zinc salt is electrolysed is in any way connected with overvoltage phenomena.

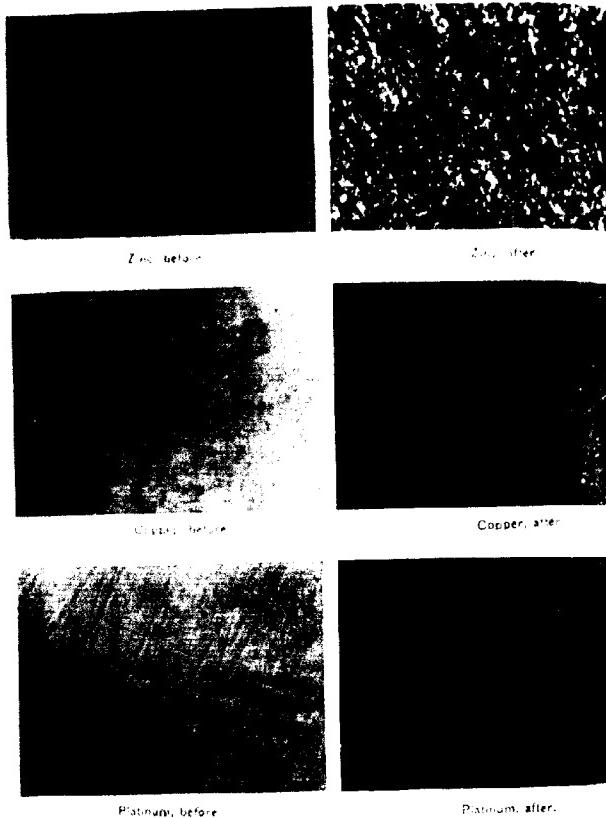
The solution used was the same as that described in Section I., the required colloid being dissolved in the stock solution as wanted.

Current densities from 100 to 600 milliamperes per sq. cm. were used, the overvoltage in all cases being nearly constant for the range.

Results were as follows:

Without colloid, overvoltage	= 0·09 volt
With 0·05 percent. of dextrin, overvoltage.....	= 0·13 ..
" 1·0 " " overvoltage.....	= 0·09 ..
" 0·02 " " gum arabic, overvoltage	= 0·08 ..
" 4·5 " " overvoltage	= 0·09 ..

A solution containing 10 per cent. of zinc as zinc sulphate, and no acid, was then used with a zinc anode instead of platinum.



Microphotographs of metal cathode plates before and after electrolysis with a current density of 1 ampere per sq. cm., for two hours. Magnification 350 diameters.

In a hydrogen electrode vessel contained 10 per cent. sulphuric acid, as before:

Without colloid, overvoltage	0.12 volt
With 0.02 per cent. of gelatin, overvoltage	0.08 "
" 20 "" overvoltage	0.12 "

The higher values in this case are partly due to the boundary potential at the junction of the zinc sulphate and sulphuric acid solutions.

(4) *Physical Changes in the Metal Surface.*—It has, of course, long been known that the nature of the surface has an important influence on overvoltage. In addition to this surface influence, it has been found by Pring (*Zeitsch. Elektrochem.*, 1913, **6**, 255) that in the case of a film of one metal deposited on another, the thickness of the film and the physical condition of the metal back ground both have an important determining effect on overvoltage. A suggestion, however, appears to have been yet made that the physical condition of the metal surface can be changed by the progress of the electrolysis.

In the present work, this was suspected to be the case when a polished platinum plate was used as cathode. After passing a heavy current through it for a short time the surface was dulled, and when the current had been passed for several hours a uniform blackening of the surface was observed, which chemical tests showed to be due to pure platinum. Similar blackening was observed at both anode and cathode if small plates or wires were used in sulphuric acid or sodium hydroxide solution, great care being taken in all cases to avoid accidental impurities.

Heavy currents (1 to 2 amperes per sq. cm.) were tried with electrodes of polished lead, zinc, and copper. In each case the metal surface became first dull and then blackened.

Microscopic examination revealed the fact that this dulling and blackening of the surface was due to extremely minute pittings in the metal, some of which when observed with slightly oblique illumination showed a peculiar craterlike form, suggesting that the surface of the metal had been blown open by an internal explosion.

Microphotographs of polished plates of platinum, copper, and zinc before and after electrolysis with a current density of 1 ampere per sq. cm. are shown in Fig. 3. As the photographs were of necessity taken with perpendicular illumination, the shape of the craters is not so well seen in the prints as it may be under the telescope itself.

(5) *The Influence of High Gaseous Pressures.*—In order to examine the effect of high pressures on overvoltage, the apparatus

shown in Fig. 2 was used in a steel enclosure capable of supporting a pressure of 300 atmospheres.

The apparatus is of glass, except the two loosely fitting stoppers which are of ebonite. Cork or india-rubber cannot be used in the pressure chamber, as it is crushed up and falls into the gas. *H* is a platinised glass electrode, which serves as a hydrogen-oxygen electrode, according to the high-pressure gas used in the chamber.

A long series of measurements was made in this way, at pressures from 1 to 100 atmospheres of hydrogen while measuring zinc overvoltage, and of oxygen while measuring the anodic voltage of platinum.

In the former case, no change of overvoltage could be detected. In the latter, a fall of about 0.02 volt appeared to be caused in two or three minutes by the application of 100 atmospheres pressure of oxygen, but if the gas is allowed to enter or escape from the pressure chamber while the galvanometer is depressed, no deflexion of the galvanometer was observed during change of pressure. The apparent change, therefore, may have been caused by variation of the oxygen electrode.

It follows from these experiments that no appreciable influence is exerted on the overvoltage by the application of a pressure of 100 atmospheres.

(6) *Measurement of the Ionisation of the Gas Liberated.*—Townsend (*J. Camb. Phil. Soc.*, 1897, **5**, 9) has shown that electrolytes carry with them a considerable electrical charge. The possibility of this charged gas exerting an effect on the potential of the vessel from which it has been liberated has up to the present been overlooked.

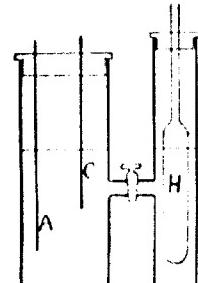
A long series of experiments was carried out, using electrodes of lead, platinum, copper, and mercury. The apparatus employed was similar to that of Townsend (*Phil. Mag.*, 1898, [v], **45**), but with the washers *A* and *B* omitted.

The following data refer to the apparatus used:

Capacity of electrometer.....	0.00005 micro-farad
... inductor	0.000017 ..
... washers.....	0.000025 ..

One volt applied to electrometer gave a deflexion of 5 divisions on the scale.

Fig. 2.



The electrolyte used in all cases was 10 per cent. sulphuric acid.

Currents from 7 to 18 amperes were used with cathodes from 1 to 15 sq. cm. area.

The conclusions drawn from a very large number of measurements are given below.

The following factors were found to affect the degree of ionisation of the gas liberated: (a) current density; (b) temperature; (c) time; (d) colloids; (e) other impurities; and (f) metal used as electrode.

(a) Changes of current density affect the degree of ionisation very little. With a lead cathode, the ionisation increased slightly when the current was doubled or the surface area of the lead doubled, but with other metals no such change could with certainty be detected.

(b) The effect of temperature is considerable, and varies with the metal used. With a lead cathode the temperature effect is very small. With a platinum cathode, heating the liquid from 20° to 60° doubled the degree of ionisation for a short time. With a mercury cathode, the ionisation was increased about 10 per cent. by a similar rise of temperature. With a copper cathode, an increase of 10 per cent. was produced by a rise in temperature of 1°, but in all cases the temperature effect is so confused with others that it is difficult to state exactly what part of the increase is due to temperature alone.

(c) Time has a large influence on the degree of ionisation of the gas. With all the solid electrodes used, the ionisation rapidly increased after the current was first started, usually attaining about half its final value in less than two minutes. After this it remained fairly constant, although a slow rise was observed after prolonged electrolysis. Interruption of the progress of electrolysis for short periods always produced a temporary rise in the degree of ionisation of gas from the solid metals, the rise being the greater the longer the interval of rest.

It should be noted that all these effects are exactly the reverse of those observed with overvoltage. With mercury, a general tendency for the gas ionisation to increase with time was observed, the rise in some cases being 50 per cent., but the behaviour of the mercury cathode is so erratic that no definite statement can be made.

(d) A very small quantity of colloid (0.1 per cent. of gum arabic) was found to lower the degree of ionisation of gas from a copper cathode to about one-third of the normal value, but the maximum lowering was only attained after the current had been passing for 200 minutes.

(e) The addition of a small quantity of copper sulphate to the electrolyte had little or no effect on the degree of ionisation of the gas from a copper cathode. 0.2 per cent. of potassium dichromate added to the electrolyte increased the ionisation of hydrogen from a platinum cathode by 25 per cent., and of oxygen from a platinum anode by 50 per cent.

(f) With a current of 8 amperes, and temperatures from 17° to 40°, the average number of divisions per minute through which the spot of light from the electrometer was deflected, is given in the following table:

Metal used.	Washers connected to electrometer.	Inductor connected to electrometer.
Platinum (cathode)	20 divisions	5 divisions
..... (anode)	8 "	2 "
Copper (cathode)	14 "	4 "
Lead "	9 "	3 "
Mercury "	6 "	2 "

Amalgamating the surface of lead or copper lowers the ionisation of the hydrogen liberated from them. Mercury shows a more erratic behaviour. On one occasion, when a current of 16 amperes was being used, deflections of 12 divisions per minute were obtained, when the washers were connected to the electrometer, in four consecutive series of readings lasting two minutes each, at three-minute intervals for cooling. Then suddenly, for no apparent reason, deflections of 32, 28, 28, 28, 28 divisions per minute were obtained. This sudden change of ionisation may be compared with the sudden changes of overvoltage of the same metal.

The relation between the ionising power of a metal and its overvoltage is remarkable.

In every case tried, where an increase in the quantity or degree of ionisation of electrolytic gas is produced, a corresponding rise of overvoltage is observed, and vice versa.

The order in which the metals employed lie with respect to their ionising power is: (1) platinum; (2) copper; (3) lead; (4) mercury. The order with respect to overvoltage is exactly the reverse of this.

The ionising power of mercury is liable to a sudden rise to a high value after using a high current density. Under these conditions, the overvoltage falls suddenly to a very low value.

Ionisation of the evolved gas is increased by rise of temperature, overvoltage is diminished.

Ionisation of the electrolytic gas from the solid metals rises rapidly after the current has been started, reaches a maximum, and then rises slowly. Overvoltage of the solid metals under the same conditions rises rapidly, reaches a maximum, and then falls slowly. A diminution in ionisation is brought about by a concomitantly with an increase in overvoltage.

It is accepted that ionisation by electrolysis is only another form of ionisation by bubbling, then, on account of the relation between the size of the bubbles and the condition of the surface from which they are liberated, the changes of ionising power due to physical changes in the metal surface, presence of colloids, temperature, etc., may be explained in all cases, excepting the often violent changes observed with mercury.

(5) *Miscellaneous Observations Made during these Experiments.* In measurements of the overvoltage of zinc when the metal was being deposited, accurate and consistent results were easily obtained, which in all cases could be reproduced to within a millivolt.

The direct potential difference, on the contrary, was liable to an error exceeding 50 millivolts.* Stirring the liquid during a measurement of true overvoltage had a very slight lowering effect. When measuring the overvoltage of lead, platinum, or mercury, the results obtained were subject to irregular variations of about millivolts with lead and platinum, and 5 to 500 millivolts with mercury. These variations are partly due to the metal being in contact with a solution containing insufficient of its own ions to balance the solution pressure of the metal. As fast as ions are taken off from the metal, they tend to be forced back again by applied E.M.F. A similar erratic potential was observed by *Ullman* (*Zeitsch. physikal. Chem.*, 1907, **59**, 148) when working with the dropping electrode, although the explanation of this phenomenon which was given was inconclusive.

The variations with mercury are so very great when a considerable current density is employed that it appears possible that an stable hydride or allotropic form of mercury is produced under these conditions.

Stirring the mercury with a glass rod decreases the overvoltage considerably when the current density is low, but increases it when the current density is high.

Conclusions.

The following conclusions may be drawn from the experimental data obtained in the present work:

(1) During electrolysis, the charged hydrogen ion penetrates through the surface into the interior of the cathode, but in order to escape as free gas after delivering its charge, breaks open the

* Many of the earlier investigators measured the direct potential difference only. Irreliable nature of this, due to the resistance of the film of gas on the surface of cathode may account for some of the erroneous conclusions arrived at by experimenters.

surface of the metal. As long as a stream of gas is escaping, the small tunnels thus formed will be kept open, but on allowing the metal to remain, many of these pores will partly close, and require additional energy to reopen them, especially as the ions can penetrate the metal deeper than at first through the partly closed tunnels.

(ii) Colloids also enter the pores in the metal surface, and their full effect on overvoltage and ionisation is not shown until they have penetrated in this way.

(iii) Hydrogen liberated in an acid solution is positively charged, and acts inductively upon the electrode, greatly lowering the overvoltage at high current densities.

(iv) Oxygen liberated in an acid solution is also positively charged, and exerts little or no effect upon the surface, which has a similar charge on it.

(v) Generally speaking, the true overvoltage of a metal is very small when the metal itself is being deposited, compared with what it is when hydrogen is being liberated.

Theories of Overvoltage. Various theories of overvoltage have been suggested by, among others, Caspari (*Zeitsch. physikal. Chem.*, 1899, **30**, 89), Nernst ("Theoretical Chemistry," English translation, 1901, p. 736), Tafel (*Zeitsch. physikal. Chem.*, 1905, **60**, 63), Böse (*ibid.*, 1909, **34**, 701), Reichstein (*Trans. Faraday Soc.*, 1914, **9**, 228), Müller (*Zeitsch. physikal. Chem.*, 1909, **65**, 1), Marie (*Compt. rend.*, 1908, **147**, 1100), and Le Blanc (*loc. cit.*, *Trans. Faraday Soc.*, 1914, **9**, 251).

A study of the above works will show that none of the present theories accounts for all the facts mentioned in the present research.

Le Blanc, by measurements with an oscillograph, has shown clearly that overvoltage observed during deposition of a metal is largely determined by chemical changes which take place during liberation of ions. He assumes that the ions are extensively hydrated.

Recent work on electromotive forces in alcohol by Lapworth and his assistants (including the author of this paper) has shown beyond doubt that the ions in an aqueous solution are strongly hydrated and therefore this assumption of Le Blanc's is fully justified. His theory will satisfactorily account for metal overvoltage, but fails in several important respects to account for many of the phenomena observed in measuring hydrogen overvoltage.

No theory of overvoltage has up to the present been suggested which will account for the great fall of overvoltage to below zero when very high current densities are used, or for the remarkable

parcellum between hydrogen overvoltage and ionisation of the liberated hydrogen.

The following theory is therefore put forward as accounting fully for all the phenomena so far observed in the study of overvoltage. *Determining Factors of Overvoltage.*—The results of the present work show that the phenomenon of overvoltage is controlled by the following factors:

(1) Supersaturation of the electrodes with gas in the molecular condition, the accumulation of this gas being brought about through the permeability of the metal to ions, and the inability of the free gas to escape except by solution or breaking the metal surface.

(2) Deficiency or excess of intermediate metastable products which are formed in the transition from the ionic to the molecular state. In view of the known fact that ions are hydrated, this intermediate product is probably the non hydrated ion.

(3) Inductive action of the escaping ionised gas bubbles on the electrode.

Of these three, the first two increase the overvoltage, while the third generally decreases it. Evidently, where no gas is being liberated, factors (1) and (3) are absent, and factor (2) alone is responsible. When gas is liberated at high current density, factor (2) completely overpowers (1) and (3). At low current density, factor (3) becomes small, but has not been found to be negligible.

According to the observations made in the present work on the solution of gas in the metal, the maximum overvoltage is largely determined by the mechanical strength of the metallic crystals at the surface, together with surface-tension forces. With solid crystals, the surface will thus tend to the same limiting, broken-up condition, whatever its original condition may be. This fact is well illustrated by Pring and Curzon's work on the overvoltage of thin wire (*Trans. Faraday Soc.*, 1912, 7, 237). The change of voltage with time in four different cases showed values which converged towards the same point.

It is evident that very high pressures are produced by the solution of gas in the electrodes, even in the case of mercury, for the surface-tension forces are considerable, but it cannot be concluded that the magnitude of this pressure is sufficient to account for the observed overvoltage on the basis of the Nernst theory, according to which in some cases pressures greater than 10^{20} atmospheres have to be admitted. From this and other considerations, Nernst's theory, which relates overvoltage to the solubility of the gas in the metal, is not a complete explanation of the observed phenomena.

Experiments with colloids showed that a penetration of the colloid into the metal takes place, and that a permanent change in the physical nature of the metal surface results. This change affected the future behaviour of the metal when used afterwards in a colloid free electrolyte. This shows that the presence of colloid has a specific effect on the electrode which determines overvoltage, in addition to the influence which Le Blanc demonstrated that the colloid possessed in affecting the velocity of hydration and dehydrogenation of ions.

The very erratic nature of the hydrogen overvoltage of mercury may be partly understood when we consider that a slight disturbance of the surface may cause great local changes in the surface-tension forces. With low current density, factor 1 is predominant. Stirring the mercury at this stage reduces the supersaturation of the surface, and the overvoltage falls. With high current density, factor 3 is predominant, the violent rush of gas tending to reduce supersaturation to a low level. Stirring the mercury at this stage, therefore, has little effect on the supersaturation, but enables the surface bubbles to escape more freely before they have acquired a positive charge sufficient to affect appreciably the potential of the metal. The overvoltage therefore rises. An intermediate stage occurs where stirring the mercury has no effect.

The sudden fall of the overvoltage of mercury to about one-quarter value at high current densities, together with the sudden rise of ionising power to about four times normal value under similar conditions, cannot be explained by the above reasoning. It seems possible that an unstable allotropic form of mercury may be produced under the influence of the electrical forces present.

Summary.

It has been shown that during the electrolysis of an acid solution with metal electrodes, the gas, before liberation, penetrates the metal surface, and on emerging breaks open the surface.

If a colloid is present, some of it is carried into the metal along with the gas.

The presence of a colloid in all cases raises the hydrogen overvoltage and diminishes the ionisation of the gas liberated. The overvoltage during deposition of a metal is affected to a much smaller degree.

The overvoltage of a metal is determined by three factors:

(1) Supersaturation of the metal surface with non-electrified, under very high pressure, due to the permeability of the metal to the ionised gas, but non-permeability to the molecular.

- (a) Deficiency or excess of non-hydrated ions in the immediate neighbourhood of the electrodes.
 (b) Inductive action of the escaping ionised gas on the electrode.
 In certain cases, factor 3 is sufficiently powerful to reduce the measured overvoltage of a metal to a negative quantity.
 The overvoltage of the metal, and the ionisation of the gas liberated from it, show an inverse relationship.

In conclusion, the author desires to express his sincere thanks to Dr. J. N. Pring for suggesting this work and for the interest he has taken in its progress.

ELECTRO-CHEMICAL LABORATORIES,
 MANCHESTER UNIVERSITY.

CXXVII.—*The Reaction of p-Benzquinone with Sulphurous Acid and with Alkali. Part I.*

By JOHN WALLIS DODGSON.

The experiments described in this paper were commenced with the intention of elucidating the action of sulphurous acid and sulphites in a solution of quinol when that solution is used as a photographic developer. On the assumption that *p*-benzoquinone is formed during development by the oxidising action of silver bromide in the presence of water, it was considered advisable to start the inquiry with an examination into the action of sulphur dioxide on a solution of *p*-benzoquinone in water at the ordinary temperature.

As is well known, the reduction of *p*-benzoquinone in aqueous solution by sulphur dioxide leads to the formation of quinol, but the yield is always less than the theoretical. The action has been considered to proceed on the lines represented by the equation:



It was also suggested by Mees and Sheppard (*Zeitsch. wiss. Photogr.*, 1902, **2**, 5) that another reaction takes place leading to the formation of dithionic acid:



EXPERIMENTAL.

A. Preliminary Experiments on the Decomposition of Dithionate.

1 g. of sodium dithionate ($\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$), when dissolved in 400 c.c. of water and boiled for half an hour with 10 c.c.

of concentrated hydrochloric acid, gave on precipitation with barium chloride 0·0235 gram of barium sulphate (0·1869 gram of crystallised sodium dithionate should yield, if completely decomposed, 0·1793 gram of barium sulphate).

(2) 0·2132 Gram of sodium dithionate, dissolved as before and evaporated to dryness with 10 c.c. of fuming nitric acid, gave a solution of the residue in water and precipitation with barium chloride, 0·1111 gram of barium sulphate (0·2132 gram of the salt when oxidised to sulphate should yield 0·4106 gram of barium sulphate).

Dithionate is therefore only partly decomposed on boiling in dilute acid, but is quantitatively oxidised to sulphate by nitric acid under the conditions of the experiments.

B. The Reduction of p-Benzquinone.

(1) In 300 c.c. of water, boiled and cooled in a current of carbon dioxide, 0·25 gram of *p*-benzoquinone was dissolved. Sulphur dioxide was then passed through until reduction was complete. The excess of sulphur dioxide was removed by evaporation, and the sulphuric acid precipitated with barium chloride, when 0·321 gram of barium sulphate was obtained.

(2) A blank experiment made without *p*-benzoquinone, but otherwise as nearly as possible identical with the foregoing, yields 0·0120 gram of barium sulphate. The sulphuric acid actually produced during the reduction of 0·25 gram of *p*-benzoquinone is therefore equivalent to 0·1211 gram of barium sulphate.

(3) The filtrate from B(1), which contained excess of barium chloride, was oxidised by evaporation to dryness with 10 c.c. of fuming nitric acid, and the residue was boiled with water and filtered, when 0·1134 gram of barium sulphate was obtained, giving a total amount of 0·5345 gram.

If one molecule of *p*-benzoquinone reacted with one molecule of sulphur dioxide, 0·25 gram of *p*-benzoquinone could give rise to the formation of 0·5394 gram of barium sulphate, and with this the total weight obtained fairly closely agrees. Dithionic acid, however, could only be formed by the interaction of one molecule of *p*-benzoquinone and two molecules of sulphur dioxide; and, judging from the experiments on the decomposition of dithionate in the presence of acid, only a small amount of this would be precipitated as barium sulphate with the first precipitate on boiling, but after oxidation with nitric acid it would be entirely precipitated as barium sulphate. Moreover, as the oxidation converts the whole of the sulphur in dithionic acid to sulphate, the effect would be to cause the total weight of barium sulphate precipitated to exceed 0·5394.

gram. The fact that the total barium sulphate was below this amount made it seem extremely probable that dithionic acid is either not formed at all or is produced in such minute quantities as to be within the limits of experimental error.

(i) As, however, dithionic acid on boiling might undergo decomposition more readily than an acidified solution of sodium dithionite, the following experiments were carried out. 0·2954 Gram of *p*-benzoquinone (1 mol.) was dissolved in 400 c.c. of air free water, and 25 c.c. of 0·2188*N* sulphurous acid (1 mol.) were added. The *p*-benzoquinone solution was completely decolorised, showing that reduction was complete; the solution had no perceptible odour of sulphur dioxide. The solution was precipitated with barium chloride, and yielded, after correction for the sulphuric acid present in the sulphurous acid, 0·4843 gram of barium sulphate. The filtrate containing excess of barium chloride was boiled for half an hour. The decomposition of dithionic acid, if it were present, would lead to the formation of a precipitate of barium sulphate. An almost imperceptible precipitate was produced. The solution was oxidised with nitric acid and evaporated to dryness. The residue yielded 0·1538 gram of barium sulphate.

(ii) The experiment was repeated, using 0·4 gram of *p*-benzoquinone instead of 0·2954 gram. Precipitation in the cold with barium chloride gave 0·4884 gram of barium sulphate; the filtrate on boiling for half-an-hour gave no perceptible precipitate, and oxidation with nitric acid yielded 0·1497 gram of barium sulphate.

The results of these experiments, particularly the complete reduction of *p*-benzoquinone with a molecular quantity of sulphur dioxide, and the absence of a weighable amount of precipitate on boiling, confirm the conclusion already arrived at, namely, that *p*-benzoquinone and sulphur dioxide react almost entirely in molecular proportions, and that dithionic acid can only be produced in very minute quantity, if at all.

Referring again to experiment *B* (3), the amount of barium sulphate precipitated before oxidation (0·4211 gram) requires for its formation 0·1952 gram of *p*-benzoquinone, that is, 78·08 per cent. of the weight taken.

(6) *The Formation of Quinol.*

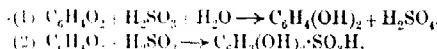
On dissolving 5 grams of *p*-benzoquinone in 400 c.c. of water, passing with a current of sulphur dioxide, and extracting several times with ether, 4·1 grams of quinol were obtained. This could be formed from 4·025 grams of *p*-benzoquinone, that is, 80·5 per cent. of the weight taken, a result which is fairly in agreement with that of the previous experiment, *B* (3).

It would seem, therefore, that two reactions take place when *p*-benzoquinone is reduced with sulphur dioxide (omitting the possible formation of minute quantities of dithionic acid). About 80 per cent. of the quinone is reduced to quinol with the accompanying oxidation of the sulphur dioxide to sulphuric acid, and the remainder forms a soluble sulphur compound not precipitable with barium chloride until after oxidation.

C. *The Nature of the Second Compound: Preparation of the Sodium Salt.*

Five grams of *p*-benzoquinone were reduced in aqueous solution by sulphur dioxide, and the product was extracted with ether. The liquid left was boiled until free from ether and sulphur dioxide, neutralised with barium carbonate and filtered, and the solution of the barium salt so obtained was carefully precipitated with sodium sulphate and again filtered. The solution of the sodium salt was evaporated to dryness under diminished pressure, and the residue washed with ether. There were thus obtained 1.77 grams of a brown, crystalline substance, which was decolorised with charcoal and recrystallised from methyl alcohol. It crystallises in almost white leaflets; in solution it gave a blue coloration with ferric chloride and other reactions characteristic of a quinol sulphonate (Seydel, *Ber.*, 1883, **16**, 688). One gram of *p*-benzoquinone, that is, 20 per cent. of the amount taken, should yield 1.96 grams of sodium quinolsulphonate (Found, SO_3^- 37.1; Na 10.91. $\text{C}_6\text{H}_4\text{O}_2\text{Na}$ requires SO_3^- 37.75. Na = 10.85 per cent.).

The reactions which take place when *p*-benzoquinone is reduced in aqueous solution by sulphur dioxide may therefore be represented as follows:



The formation of quinolsulphonic acid when quinol is oxidised by silver bromide in the presence of sulphite was suggested by Bogisch (*Phar. Korresp.*, 1900, 93) and by Andresen (*ibid.*, 1904, 185), but was questioned by Lüther and Leubner on the ground that "ring substitution of the SO_3H group in the benzene nucleus is possible only at a very high temperature and by the use of strong sulphuric acid" (Leubner, *Diss.*, Dresden, 1912). This view is, of course, correct as regards the direct sulphonation of quinol with sulphuric acid. The reaction in the case now being considered is, however, essentially different, as *p*-benzoquinone and sulphuric acid are the reagents concerned. It is an instance of "indirect"

"Addition" similar to that which leads to the formation of chloroquinol when concentrated hydrochloric acid acts on *p*-benzoquinone.

The formation of quinolsulphonic acid in developing solution during use has been confirmed by Pinnow (*Zeitsch. wiss. Photo-*, 1913, **13**, 41), who has isolated the sodium salt from a used developer.

The formation of both sulphuric acid and quinolsulphonic acid, in the reduction of *p*-benzoquinone by sulphur dioxide, supports the hypothesis that a sulphurous acid solution contains molecules of each of the forms:



and suggests that the former may lead to the formation of quinol and sulphuric acid, and the latter to that of the sulphonate acid, the relative amounts of each product being determined (a) by the proportion of each form present in the sulphurous acid, (b) the relative velocities of the two reactions, and possibly by other factors. The point, together with the constitution of sulphurous acid, is being further investigated in this laboratory.

In the experiments which follow, solutions of sulphur dioxide of known strength were employed instead of the gas, and in estimating the sulphuric acid formed, correction was made in all cases for the small amount of sulphuric acid present in these solutions.

(1) Effect of Variation of Temperature.

Four experiments were made at 0°, room temperature (about 20°), 20°, and 50° respectively. The sulphur dioxide solution used was 57.6%. The water was well boiled and cooled in a current of

TABLE I.

Temperature.	<i>A.</i> <i>p</i> -Benzo- quinone solution	<i>B.</i> Sulphur dioxide solution. c.c.	Barium sulphate		
			from sulphuric acid formed	from sulphonic acid	Total. Gram.
0°	0.25 gram in 100 c.c. of water (added to <i>B</i>)	50 with 250 c.c. of water	0.4167	0.1167	0.5334
20°	0.25 gram in 375 c.c. of water	25 (added to <i>A</i>)	0.4166	0.1167	0.5333
50°	0.25 gram solid (added to <i>B</i>)	50 with 350 c.c. of water	0.4221	0.1172	0.5393
50°	0.25 gram solid (added to <i>B</i>)	50 with 350 c.c. of water	0.4273	0.1153	0.5426

carbon dioxide, which was also allowed to pass through the apparatus throughout each experiment. The sulphur dioxide used was always in excess of that actually required to reduce the amount of *p*-benzoquinone taken.

From the results shown in table I it is obvious that change of temperature within the limits taken is practically without effect on the relative amounts of sulphate and sulphonate produced.

(2) *Reduction in the Presence of Hydrochloric Acid.*

TABLE II.

<i>p</i> -Benzoquinone solution.	Concentrated hydrochloric acid.		Sulphur dioxide solution.	Barium sulphate		
	c.c.	c.c.		sulphate.	from sulphate.	Total Gram.
0.25 gram in 375 c.c. of water	none	25	0.4166	0.1167	0.5333	
0.25 gram in 275 c.c. of water	100	25	0.4142	0.1153	0.5255	
0.25 gram in 175 c.c. of water	200	25	0.0374	0.0112	0.0486	

The *p*-benzoquinone was dissolved in the stated quantity of water, and the acid added; this was followed by the addition of the sulphur dioxide solution, when in each case the yellow colour of the *p*-benzoquinone solution was immediately discharged. It is obvious, however, that much hydrochloric acid greatly affects the course of the reaction. That this is due to the formation of chloroquinol was proved by dissolving 5 grains of *p*-benzoquinone in 200 c.c. of water and adding 400 c.c. of concentrated hydrochloric acid. Chloroquinol was easily extracted from the liquid with ether.

E. *Reduction of p-Benzoquinone in the Presence of Alkali Hydroxide.*

(1) A series of experiments was carried out with varying amounts of alkali, and the results obtained are shown in the tables below.

In each experiment the volume of alkali (0.3080*N*-sodium hydroxide) stated in the table was placed in a flask with water, making together 275 c.c.; 25 c.c. of sulphur dioxide solution (0.2734*N*) was then added, followed by the *p*-benzoquinone in 100 c.c. of water. The mixed solutions were acidified after remaining about five minutes with 10 c.c. of concentrated hydrochloric acid, and the excess of sulphur dioxide was boiled off. As the sulphur dioxide was always in excess of the amount required to reduce the quinone, slight variations in the strength of the solution used had no effect on the results obtained. The solution was, however, standardised

from time to time, and estimations of the amounts of sulphuric acid present in it were made. The figures given in the tables have been corrected accordingly.

TABLE III.

Mols. alkali to 1 mol. SO ₂	Colour on adding <i>p</i> -benzoquinone.	Colour on acidifying.	Barium sulphate		
			from sulphate Gram.	from sulphonate Gram.	Total Gram.
0.0	colourless	no acid added	0.4166	0.4167	0.8333
0.5	"	colourless	0.4162	0.4084	0.5246
1.0	"	"	0.4150	0.4070	0.5220
1.5	very pale yellow	nearly colour- less	0.0172	0.4291	0.4463
2.0	bright green changing to yellow	very pale yel- low	0.0166	0.3085	0.3251
2.5	red-brown	yellow	0.0191	0.2162	0.2353
3.0	dark red-brown	brownish-yellow	0.0182	0.1992	0.2174
4.0	dark brown	yellow-brown	0.0207	0.1897	0.2104
6.0	very dark brown	yellow-brown	0.0183	0.1884	0.2067

The above results show that as long as the alkali present is not larger in quantity than is required to form sodium hydrogen sulphite with the sulphur dioxide used, the reactions proceed on practically the same lines as in the total absence of alkali, but that when this amount is exceeded there is more than a reversal of the amounts of barium sulphate obtained, nearly the whole of the precipitate being formed after oxidising with nitric acid, whilst the barium sulphate precipitated before oxidation sinks to a small and almost constant quantity. Independent experiments showed that the solutions obtained with excess of alkali, after acidifying with sulphuric acid, neutralising with barium carbonate, and filtering give the blue colour with dilute ferric chloride solution indicative of the presence of the sulphonate.

It is noticeable from the above that the gradual addition of alkali leads to a continual decrease in the amount of sulphate precipitated after oxidation, suggesting a progressive destruction of the quinone, and the following experiments were carried out with the intention of measuring the extent of this destruction by estimating its residual activity, as regards oxidising and sulphonation, after treatment with alkali.

(2) To 0.25 gram of *p*-benzoquinone in water, 0.3080*N* sodium hydroxide solution was added; the action of the alkali was then checked as quickly as possible by the addition of 10 c.c. of concentrated hydrochloric acid, and 25 c.c. of 0.2726*N* sulphur dioxide solution were added. The total volume of the mixture was then 400 c.c., as in the previous series of experiments. The excess of

sulphur dioxide was boiled off, and the sulphate estimated before and after oxidation. A current of hydrogen was kept passing through the apparatus until the excess of sulphur dioxide had been removed.

The results were as follows:

TABLE IV.

Molecular proportions of NaOH to SO ₂		Barium sulphate		
NaOH.	SO ₂ .	from sulphate Gram.	from sulphonate Gram.	Total Gram.
None.		0.4166	0.1167	0.5333
1 Mol.	1 Mol.	0.1806	0.0373	0.2179
1/2 "	"	0.1727	0.0353	0.2080
2/3 "	"	0.1484	0.0256	0.1740
5 "	"	0.1437	0.0211	0.1648

(3) *Effect of Time.*

To 0.25 grain of *p*-benzoquinone in 350 c.c. of water, 33 c.c. of 0.3080*N* sodium hydroxide were added, and the solution was allowed to remain in an atmosphere of hydrogen for forty-eight hours; it was then acidified, and 25 c.c. of 0.2721*N*-sulphur dioxide solution were added (molecular proportion NaOH to SO₂ of approx.). The weight of barium sulphate obtained before oxidation was 0.0014 gram, and after oxidation 0.0085 gram, giving a loss of 0.0099 gram.

From the above series of experiments it appears that:

(i) The addition of alkali hydroxide diminishes very materially both the oxidising power of a solution of *p*-benzoquinone and also the formation of sulphonic acid.

(ii) The action of the alkali, although rapid in its earlier stages is not instantaneous, and on prolonged action further changes take place which almost totally prevent both oxidation and sulphonation.

Here it may be noted that Mees and Sheppard (*loc. cit.*) state that alkali hydroxide acts on *p*-benzoquinone with the formation of quinol and hydrogen peroxide. They were able to obtain the usual blue colour reaction with acidified dichromate, and they represent the reaction by the equation:



The reaction has been questioned by M. A. Gordon (*J. phys. Chem.*, 1913, **17**, 1) and by Lüther and Leubner (*loc. cit.*), who suggest a totally different action. Up to the present the author has not been able to repeat Mees and Sheppard's observations. Moreover, it is difficult, by means of their hypothesis, to account for the great reduction in the oxidising power of *p*-benzoquinone resulting from the action of alkali. The equation given by Mees

Sheppard would suggest that this oxidising power should be increased, owing to the substitution of some of the *p*-benzoquinone by its equivalent of hydrogen peroxide, and at the same time the amount of sulphonate produced should be diminished owing to the conversion of the quinone into quinol. It is possible that some disulphonate might be formed, but this it produced at all would only be in very minute quantities (*Nahl. Monatsh.*, 1901, **22**, 737). The results given in table IV, however, show a considerable decrease in the production of sulphate, although the ratio of sulphate to sulphonate actually increases from slightly less than 4:1 when no alkali is used to somewhat more than 7:1 with five molecules of alkali to one of sulphur dioxide. In view, therefore, of the complex nature of the conditions under which the reactions take place, the results obtained (tables III and IV) do not appear to render possible at present the formation of any satisfactory hypothesis as to the nature of the action of alkaline sulphite or of alkali on *p*-benzoquinone. Further experiments are in progress, the results of which will be communicated later.

Summary.

- (1) When *p*-benzoquinone is reduced by sulphurous acid, quinol, sulphuric acid, and quinolsulphonic acid are formed; the sulphonic acid to an extent equivalent to about 20 per cent of the *p*-benzoquinone employed.
- (2) The reaction is not affected by reasonable amounts of hydrochloric acid, but is strongly inhibited by large quantities, owing to the formation of chloroquinol. It is also not materially affected by temperature.
- (3) When *p*-benzoquinone is reduced with alkaline sulphite the reduction of the sulphonate is greatly increased, whilst the sulphite formed sinks to a very small and almost constant quantity.
- (4) Further addition of alkali leads to a diminution in the amount of sulphonate formed, without any increase in the amount of sulphate produced.
- (5) Prolonged action of the alkali almost completely prevents both reactions.
- (6) Dithionic acid, if formed at all, is produced in very minute quantity.

I wish to thank Prof. H. Bassett for suggesting this work and for his interest in it.

CXCVIII.—*The Rate of Combination of Gaseous Nitric Oxide and Chlorine. Part I.*

By JOSEPH EDWARD COATES and ADA FINNEY.

The direct union of nitric oxide and chlorine was first observed in 1848 by Gay Lussac (*Ann. Chim. Phys.*, [iii], **23**, 203), who proved the composition of the orange-coloured gaseous product by measuring the contraction that took place when two bulbs containing nitric oxide and chlorine respectively were put in communication with each other. The decrease of pressure was observed by means of a mercury manometer attached to the nitric oxide bulb, but no mention was made of the rate of contraction. A repetition of this rough experiment showed that the velocity of the reaction was sufficiently slow at the ordinary temperature to be quantitatively followed.

The accurate measurement of this reaction velocity is clearly of considerable interest and importance. According to the equation



the reaction should be one of the third order. The number of reactions of which the kinetics have been thoroughly studied is by no means large; only a very few have been stated to be of the third order, and these are for the most part reactions which proceed at high temperatures and are subject to irregularities due to the influence of the walls of the containing vessel.* The oxidation of nitric oxide at the ordinary temperature was found by Bodenstein and Meinecke (*Zeitsch. Elektrochem.*, 1910, **16**, 1) to be a gas reaction of the third order.

The interaction of nitric oxide and chloride, being rapid at low temperatures, is likely to be "pure" and free from irregularities. Further, like many reactions in which chlorine takes part, it may be photosensitive. Briefly stated, the chief result of the experiments described in this communication is that the reaction is of the third order, when measured at the two temperatures, 0° and 14.8°.

At the time this investigation was begun (January, 1913), the authors were not aware of any recent work on the subject, so the results given in this paper formed the subject of a thesis presented in June, 1913, to the University of Birmingham. Prof.

* See, for example, Bodenstein (combination of hydrogen and oxygen), *Ztsch. physikal. Chem.*, 1899, **29**, 665; Bodlander and Koppé (oxidation of carbon dioxide), *Zeitsch. Elektrochem.*, 1903, **9**, 559; Kuhl (oxidation of carbon monoxide), *Zeitsch. physikal. Chem.*, 1903, **44**, 385.

cation was deferred until the work had been brought into a more complete state. Quite recently, however, the authors' attention has been called to a paper by M. Trautz (*Zeitsch. Elektrochem.*, 1914, **20**, 325, (abstract); *Sitzungsber. Heidelberger Akad. Wiss., Abt. A, Abh. 1, Jan.*, 1914), who has, it appears, also investigated the velocity of formation of nitrosyl chloride. He quotes, further, some work on the same subject by Kiss Arpád ("A nitrogen oxyd és chlor egymásra hatásának sebességeiről," *Diss.*, Budapest und Magyar Chemikusok, Lajja, 1913. Evi 7-8), whose paper has appeared in the Hungarian language only. Both of these investigators arrive at the same general conclusion as the authors, namely, that the reaction is termolecular; it appeared, therefore, advisable to publish at once the first results, reserving those of the experiments now in progress for a second communication.

EXPERIMENTAL.

In principle the method adopted was as follows: A known quantity of nitric oxide was injected very rapidly through a capillary tube into a bulb containing a known quantity of chlorine. This bulb was connected with a protected mercury manometer, so that the rate of diminution of pressure at constant volume could be easily measured. The use of a mercury manometer is, of course, rendered difficult by the fact that chlorine and nitrosyl chloride spidily attack mercury. Protection by a short column of syrupy phosphoric acid or sulphuric acid was unsatisfactory as the liquid not only retarded the motion of the mercury but also did not completely protect it. The interposition of a cushion of nitrogen between the reaction bulb and manometer was found to afford a much better, although not a complete, protection. The best way out of this difficulty lies in the employment of a quartz manometer free from mercury, and this plan has been adopted in the most recent experiments (not described in this paper).

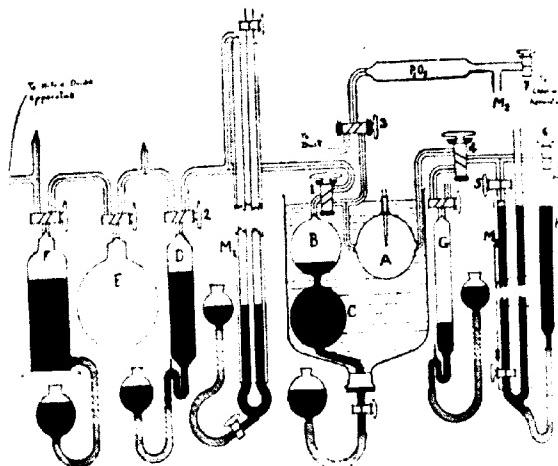
For the lubrication of stopcocks in contact with the reactive gas both phosphoric acid (prepared by Chapman and Ged's method, T., 1911, **99**, 1736) and a special lubricant recommended by Guye* (*J. Chim. Phys.*, 1908, **6**, 756) and by Wourtzel (*J. Chim. Phys.*, 1913, **11**, 31) were used. The latter consisted of a mixture of paraffin and stearin which had been repeatedly saturated with chlorine and heated in a vacuum; although it required fairly frequent renewal it had the advantage of allowing one to turn the stopcocks more quickly than could be done with phosphoric acid. Further, phosphoric acid was not entirely free from attack.

Preparation of Gases.—The chlorine was prepared from pure

* We are indebted to Prof. P. A. Guye for a small sample of this lubricant.

potassium permanganate and hydrochloric acid, washed with potassium permanganate solution, copper sulphate solution, and concentrated sulphuric acid, and finally dried by means of phosphoric oxide.

The nitric oxide was prepared by dropping 50 per cent. sulphuric acid into a concentrated solution of potassium iodide and sodium nitrite in molecular proportions. Acid impurities were removed by passing the gas through concentrated potassium hydroxide solution and over the solid alkali, and it was finally dried by phosphoric oxide. Owing to the impossibility of storing nitric oxide over water, with which it reacts with the formation of nitrogen (*Müller, Zeitsch. anal. Chem.*, 1911, **50**, 401), it was collected in a 3 litre



glass balloon (*E*). After repeatedly exhausting the general apparatus and balloon and washing out with nitric oxide, the gas was passed into a mercury gas-holder (*F*), from which it was taken into the balloon until the pressure in the latter was about 1½ atmospheres.*

Description of the Apparatus.—The reaction vessel *A* consisted of a glass bulb of 240·5 c.c. capacity, at the centre of which was situated a thermocouple of platinum and platinum-rhodium alloy, the wire being completely protected by a very thin layer of glass. The couple was connected in the usual way with a sensitive moving

* A freshly made solution of ferrous sulphate absorbed 99·9 per cent. of a 25% of this gas.

coil galvanometer, and the spot of light moved over about 20 scale divisions for a temperature difference of 1° . Although the bulb was kept in melting ice, the temperature always rose rapidly to a maximum on mixing the gases, then gradually fell again. A glance at the tables will show the general course of the temperature change. The temperature at the centre of the bulb rises somewhat higher than that at the cold walls; however, in the calculations a uniform temperature equal to that at the centre has been assumed.

The bulb *A* was connected by the shortest possible length of capillary tubing through a mercury-protected three-way stopcock 1 to a pair of glass bulbs, *B* and *C*, of which *C* was slightly the larger. The volume of *B* from the stopcock to a mark on the tube connecting *B* and *C* was 211.0 c.c. The bulb *C* was interposed between *B* and the mercury reservoir in order that the mercury entering *B* should not warm the gas above it. The bulbs *A*, *B*, *C* were completely immersed in a bath of water or melting ice, whilst the capillary between *B* and *C* was almost entirely immersed. The third arm of the three way stopcock 1 was connected with a mercury manometer *M*₁, and through a three-way stopcock 2 with a reservoir *D*, which served to adjust the pressure in *B* to any desired value. *D* was further connected as shown with the balloon *E* of nitric oxide, which was joined to the auxiliary reservoir *F* and the apparatus for generating nitric oxide. For the admission of chlorine to the bulb *A*, a branch capillary led from that connecting *A* and *B* through a three way stopcock 3 and a tube of phosphoric oxide to a mercury manometer *M*₂ (not drawn in the figure), protected from attack by a layer of concentrated sulphuric acid, and then to the apparatus for generating and purifying chlorine. The reaction bulb *A* was further provided with a capillary exit which served for exhaustion and for measuring the pressure of the reacting gases. It was connected with a three way stopcock 4, one arm of which led to a reservoir of nitrogen *G*, whilst the other was joined to a mercury manometer, *M*₃, and a Toepler pump protected by mercury and sticks of potassium hydroxide. The manometers had a bore of 7 mm., and were provided with mirror sides. After fitting together, the apparatus was well dried by heating and long-continued washing with dry air under diminished pressure.

After exhausting, washing out with nitric oxide, and sealing off the tube connecting *E* and *D*, and filling the system *D*, *M*₁, *B*, *C* with mercury, nitric oxide was passed into *D*, and thence into *B*. The mercury surface was fixed at the mark on the tube joining *B* and *C*, and the pressure in *B* adjusted to the required value by drawing the mercury in *D*.

Generation of chlorine was begun several hours before the commencement of an experiment; it was allowed to escape at the stopcock 3, and a sample of the gas (about 70 c.c.) taken immediately before an experiment was completely absorbed by concentrated aqueous potassium hydroxide. The bulb A and connecting tubes (previously well dried) were exhausted several times and washed out before finally filling with chlorine, the stopcock 5 being closed and M_3 completely filled with mercury. For the purpose of adjusting the pressure of chlorine in A, 4 being closed, 3 was opened, then 7 was very carefully opened until the pressure as indicated by M_3 was that desired or slightly in excess thereof; in the latter case the pressure could be reduced to the correct value by very slightly opening 4 and 6, 3 being now closed. The space between 4, 6, and 5 was then exhausted and filled with nitrogen from B . The pressure in A was finally checked by fixing the pressure of the nitrogen at the value that should obtain in A (5 and 8 being open), and then putting A and M_3 into communication through 4; no movement of the mercury in M_3 should be observed. After closing 4 the pressure above M_3 was adjusted as nearly as possible to the value that would obtain in A after the addition of nitric oxide and at the time observations of the diminishing pressure would be commenced. A fair approximation could be made after a little experience. The mercury meniscus in M_3 was not more than 5 mm. from the capillary continuation, so that the dead space containing nitrogen had a volume of not more than about 0.5 c.c. B having been filled with nitric oxide at known pressure as previously described, mercury was allowed to enter the bulb until the pressure was nearly two atmospheres. Then, at a given time when B and A were put into communication through 1, nitric oxide was thus very rapidly injected into A, and after a little practice the rising mercury in B could be stopped in the capillary near the stopcock, which was quickly closed.

This process of mixing occupied as a rule about ten to fifteen seconds. The "time of mixing" ($t=0$) was taken as the mean of the times of opening and closing the stopcock 1. However, the indefiniteness in the "time of mixing" became inappreciable at the time at which trustworthy pressure measurements were commenced.

Immediately after closing 1, 4 and 5 were opened, then 8 was very carefully opened slightly, the direction in which the meniscus began to move noted, and the reservoir H quickly adjusted until position was found such that 8 could be completely opened without causing a movement of the meniscus of more than one or at most two mm. from its initial position. Then, as the pressure of A decreased, so the reservoir H was steadily lowered in such a way

that the mercury meniscus below 5 remained in a fixed position; this could be done quite satisfactorily after a little practice. Readings of the right-hand limb of the manometer were begun as early as possible (usually about a minute after mixing), and taken throughout at given time intervals. Another observer took time and temperature readings. When the mercury meniscus began to show signs of corrosion, the gas above it was rapidly replaced by nitrogen by closing 4 and 8, exhausting, admitting nitrogen from G, and finally reducing the pressure to that which obtained in A (estimated by extrapolation). Stopcock 4 was then opened again, and pressure readings continued. This operation was usually repeated two or three times during one experiment.

In the experiments here recorded the nitric oxide and chlorine were taken in equivalent proportions (two molecules of nitric oxide to one of chlorine). The initial partial pressure of the chlorine was about a third, whilst that of the nitric oxide was about two-thirds of an atmosphere, so that the initial concentrations of the two gases from the point of view of the law of mass action were equal, namely, a third of an atmosphere. Velocity constants were calculated by means of the integrated equations for reactions of the first, second, and third orders, namely,

$$K_1 = \frac{1}{t} \log \frac{p_0}{p}; K_2 = \frac{1}{t} \frac{p_0 - p}{p_0 p}; K_3 = \frac{1}{2t} \left(\frac{1}{p^2} - \frac{1}{p_0^2} \right),$$

where p_0 is the initial partial pressure and p the partial pressure of the chlorine at any time t . The pressure loss π is equal to the difference between the initial total pressure (P_0) and the total pressure observed at any time (P), ($\pi = P_0 - P$), and the partial pressure of the chlorine at that time is $p = p_0 - \pi$.

In this method of procedure the validity of the simple gas law has been tacitly assumed; this introduces a slight error in the case of the chlorine, and a somewhat greater one as regards the nitrosyl chloride, but in this series of experiments they have been neglected commensurate with the experimental errors.

The observed total pressure was corrected from the observed temperature to that of the bath before using for the calculation of the velocity constant. The following four tables give the results of three experiments at 0° and one at 14.8°. The second column gives the temperature indicated by the thermocouple, and the last gives the percentage (x) of the reaction completed ($x = 100\pi/p_0$). There is reason to believe that the results expressed in table I are somewhat less trustworthy than those that follow.

TABLE I.

Vol. of bulb A = 240·5 c.c. Temperature = 0°.

Vol. of bulb B = 205·0 c.c. Barometer = 753·4 mm.

Pressure of nitric oxide in B = 593·3 mm.

Initial pressure of chlorine in A = 252·8 mm.

Initial pressure of nitric oxide in A = 505·7 mm.

<i>t</i> (min.).	<i>T</i> °	<i>P</i> mm.	<i>p</i> mm.	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_3 \times 10^4$	$\frac{K_3}{K_1}$
0·0	0·0	[753·3]	[252·8]	—	—	—	—
2·3	3·9	676·4	161·3	8·5	9·8	4·95	36
3·0	3·1	662·9	149·9	7·6	9·0	4·81	41
3·75	2·5	651·9	140·3	6·8	8·4	4·70	44
4·5	2·15	642·9	132·2	6·3	8·0	4·62	45
5·5	1·8	633·5	123·5	5·7	7·5	4·54	43
6·75	1·5	623·4	114·3	5·1	7·1	4·51	43
8·5	1·1	612·5	104·2	4·5	6·6	4·50	49
11·0	0·8	602·0	94·2	3·9	6·0	4·41	63
14·0	0·7	592·5	85·1	3·4	5·6	4·37	66
17·0	0·5	584·5	77·7	3·0	5·2	4·41	69
20·0	0·45	574·4	71·7	2·7	5·0	4·47	71
27·0	0·3	568·5	62·2	2·3	4·5	4·50	71
46·0	0·2	552·6	46·4	1·6	3·8	4·88	7
67·0	0·1	543·3	37·3	1·2	3·4	5·23	7

TABLE II.

Vol. of bulb A = 240·5 c.c. Temperature = 0°.

Vol. of bulb B = 211·0 c.c. Barometer = 749·1 mm.

Pressure of nitric oxide in B = 578·0 mm.

Initial pressure of nitric oxide in A = 507·1 mm.

Initial pressure of chlorine in A = 253·6 mm.

<i>t</i> min.	<i>T</i> °	<i>P</i> mm.	<i>p</i> mm.	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_3 \times 10^4$	$\frac{K_3}{K_1}$
0·0	0·0	[760·7]	[253·6]	—	—	—	—
3·0	2·8	672·1	156·8	6·9	8·1	4·19	3
3·5	2·4	665·1	152·2	6·4	7·5	3·95	6
4·25	1·95	653·1	141·2	5·9	7·4	4·08	6
8·5	1·05	619·4	110·8	4·2	6·0	3·88	7
9·5	0·9	614·0	105·1	4·0	5·9	3·95	7
12·5	0·7	602·9	94·2	3·4	5·3	3·90	6
14·5	0·6	597·9	87·6	3·2	5·1	3·96	6
18·5	0·5	585·8	77·7	2·8	4·8	4·05	6
22·5	0·4	579·2	71·4	2·4	4·5	4·01	5
26·5	0·3	573·7	65·9	2·2	4·2	4·06	5
32·5	0·25	566·5	58·8	2·0	4·0	4·20	5
40·5	0·2	560·3	52·8	1·7	3·7	4·23	5
59·0	0·2	550·4	42·9	1·3	3·3	4·55	5
72·5	0·1	545·4	38·0	1·1	3·1	4·66	5

TABLE III.

Vol. of bulb A = 240·5 c.c. Temperature 0°.

Vol. of bulb B = 211·0 c.c. Barometer 751·3.

Pressure of nitric oxide in B = 584·0 mm.

Initial pressure of nitric oxide in A = 512·3 mm.

Initial pressure of chlorine in A = 255·3 mm.

Time, min.	T°	P, mm.	p, mm.	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_3 \times 10^4$	per cent.
0·0	0·0	[767·6]	[255·3]	—	—	—	0
3·0	2·75	676·1	156·2	7·1	8·3	4·27	39
3·5	2·85	666·0	148·2	6·7	8·3	4·31	42
4·5	1·80	652·0	138·2	6·1	7·8	4·37	47
5·0	1·85	647·0	130·7	5·8	7·4	4·32	49
6·0	1·35	638·5	122·8	5·3	7·0	4·25	52
8·0	1·00	624·5	109·9	4·5	6·5	4·21	57
10·0	0·75	613·8	99·7	4·1	6·1	4·26	61
12·0	0·65	606·3	91·0	3·7	5·8	4·32	64
13·0	0·50	598·3	82·9	3·3	5·4	4·35	68
20·0	0·35	584·8	71·7	2·8	5·0	4·47	72
31·0	0·20	571·0	58·2	2·1	4·2	4·51	77
37·0	0·10	555·0	42·5	1·4	3·3	4·70	83

TABLE IV.

Vol. of bulb A = 240·5 c.c. Temperature 14·8°.

Vol. of bulb B = 211·0 c.c. Barometer 755·3 mm.

Pressure of nitric oxide in B = 582 mm.

Initial pressure of nitric oxide in A = 510·6 mm.

Initial pressure of chlorine in A = 255·3 mm.

Time, min.	T°	P, mm.	p, mm.	$K_1 \times 10^4$	$K_2 \times 10^4$	$K_3 \times 10^4$	per cent.
0·0	14·8	[765·9]	[255·3]	—	—	—	0
1·5	20·5	698·3	174·3	11·1	12·1	5·86	32
2·0	18·3	681·5	162·6	9·8	11·0	5·62	36
3·0	17·0	658·3	142·7	8·4	10·0	5·62	44
4·0	16·4	641·5	127·3	7·6	9·8	5·80	50
5·0	15·7	621·8	109·3	6·1	8·7	5·70	57
9·0	15·3	603·3	91·6	4·9	7·7	5·77	64
14·0	15·0	587·5	76·2	3·8	6·6	5·80	70
20·0	14·8	574·5	63·7	3·0	5·9	5·78	75
24·0	14·8	564·7	54·1	2·4	5·2	5·82	79
38·0	14·8	535·1	24·5	0·9	3·1	7·00	90

Trustworthy readings could not as a rule be made during the first third of the reaction on account of its rapidity. The values of K_1 and K_2 show a distinct drift throughout, whilst those of K_3 remain very fairly constant until about three-quarters of the reaction is over, when they begin to increase. Assuming the reaction to be of the third order, this increase in the constant indicates that the pressure in A is decreasing too rapidly; for example, in table III, at 31 minutes $P(\text{corr.}) = 570·5$ mm., whereas assuming $K_3 = 4·3 \times 10^{-6}$, it should be 572 mm. This is doubtless due to attack of the mercury, which, in spite of the precautions described,

could not be entirely avoided; this effect naturally became more marked in the later stages of the reaction, and the constants began to increase at about the time when the mercury showed distinct signs of attack. Further, towards the end of the reaction the walls of the manometer tube in the neighbourhood of the mercury meniscus became dirty, making it more difficult to keep the meniscus at a fixed position. Owing to these disturbances satisfactory readings for the end of the reaction could not be obtained. Combination may be assumed to proceed to completion at the low temperatures employed. Only one trustworthy set of readings was obtained at a temperature above zero, namely, at 14·8°.

The mean values of the constants may be taken to be $5\cdot7 \times 10^{-3}$ at 14·8°, and $4\cdot2 \times 10^{-3}$ at 0°, expressed in units of mm. of mercury and minutes. They may be converted into units of gram-molecules per litre by means of the equation $VP/760 = nRT$, so that $n = P/760 \times 0\cdot0827$, where P is expressed in mm. of mercury, and V denotes volume in litres. The factor for converting K into units of molecules per litre is $(760 \times 0\cdot0827)^2$, and in these units K has the values 1216 and 1820 at 0° and 14·8° respectively. The constant is not in agreement with that given by Kiss Arpad (*loc. cit.*), who found $K_2 = 0\cdot262 \times 10^{-3}$ at 18° (in units of mm. of mercury). From the above-mentioned values of K it appears that the temperature coefficient is very small (about 1·23 for an increase of temperature of 10°), and in consequence the effect on the reaction velocity of initial rise of temperature on mixing the gases is small. Trautz (*loc. cit.*) has calculated that, according to his theory of reaction velocities, the temperature-coefficient should lie between 0·93 and 1·44, and he considers the most probable value to be 1·17, which is in fair agreement with the experimental number given above.

Further experimental work is in progress which has for its object the more accurate determination of the velocity constant under varying conditions of temperature and concentration, and a study of the effect of light, of extreme dryness, and of the walls of the vessel. Special attention has been given to the purity of the gases, which have been prepared by fractionation of the liquids and for pressure measurements a sensitive quartz spiral manometer has been constructed.

In conclusion, the authors wish to express their indebtedness to the Chemical Society for a grant which partly defrayed the cost of the research.

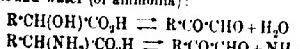
THE CHEMICAL LABORATORIES,
UNIVERSITY OF BIRMINGHAM.

CXXIX.—*A General Method for the Preparation of Glyoxals and their Acetals.*

By HENRY DRYSDALE DAKIN and HAROLD WARD DUDLEY.

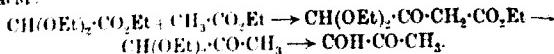
ONLY a few representatives of the group of α -ketonic aldehydes or glyoxals have been hitherto prepared, and no method of wide applicability for their synthesis has been described. Glyoxal itself has been obtained by Harries (*Ber.*, 1907, **40**, 165) as a yellowish-green substance on distilling with phosphoric oxide the crude polymerised product derived from the oxidation of acetaldehyde or similar substances. The acetal of methylglyoxal was prepared by Wehl and Lange (*Ber.*, 1908, **41**, 3612) by treating the piperide of ethyl diethoxyacetate with magnesium methyl iodide. This substance on hydrolysis with dilute sulphuric acid was shown by Meisenheimer (*Ber.*, 1912, **45**, 2635) to yield methylglyoxal, which was eventually isolated as an intensely yellow, volatile liquid readily undergoing polymerisation. *iso*Propylglyoxal was obtained by Conrad and Ruppert (*Ber.*, 1897, **30**, 862) by heating the acid $\text{COH-CO:CMey}_2\text{CO}_2\text{H}$ with water. Phenylglyoxal was prepared by von Pechmann (*Ber.*, 1887, **20**, 2904) by hydrolysing with dilute sulphuric acid the product of the action of sodium hydrogen sulphite on oximeacetophenone, whilst by the same method phenylglyoxal was obtained by Müller and von Pechmann (*Ber.*, 1889, **22**, 2560). It is a curious fact that the synthesis of phenyl glyoxal is frequently unsuccessful owing to the production of large quantities of a compound believed by Pinner (*Ber.*, 1902, **35**, 4134) to be 2-benzoyl-5-phenylglyoxaline-1-sulphonic acid. The conditions necessary for success do not appear to be completely known. These various methods which have been employed for the preparation of glyoxals do not appear to be generally applicable for the preparation of other homologous glyoxals. The authors have recently adduced evidence tending to show that glyoxals may play a rôle in the intermediary metabolism of plant and animal cells, and it became desirable to devise a method for the convenient synthesis of these compounds. It has been shown that α -amino- and α -hydroxy-acids on digestion in dilute aqueous solution with *p*-nitrobenzylhydrazine give the bis-*p*-nitrophenylhydrazone of the corresponding glyoxals (*J. Biol. Chem.*, 1913, **15**, 127), but this reaction is totally unsuited for the preparation of the glyoxals themselves.*

* We have assumed in this reaction that the hydroxy-(or amino-)acids dissociate fully into glyoxals and water (or ammonia):



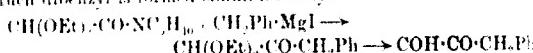
A convenient method for the synthesis of most glyoxals and their acetals is based on the preparation of ethyl γ -diethoxyacetacetate. This ketonic ester is readily obtained in excellent yield by the condensation of ethyl diethoxyacetate and ethyl acetate by means of sodium.

On hydrolysing ethyl γ -diethoxyacetacetate with dilute aqueous potassium hydroxide the acetal of methylglyoxal is readily obtained, which in turn gives methylglyoxal on boiling with dilute sulphuric acid:

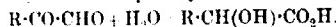


Ethyl γ -diethoxyacetacetate is readily substituted by one or two alkyl groups by successive treatment with sodium and alkyl haloids and from the resulting substituted esters we have prepared a variety of glyoxals and their acetals in satisfactory yields.

Since phenyl haloids do not react readily with the sodium derivatives of acetoacetic esters, it appeared improbable that benzylglyoxal could be prepared by this method of synthesis. Accordingly we have synthesised this substance (*J. Biol. Chem.*, 1914, 18, 42) by a modification of Wohl and Lange's method by treating the piperidide of ethyl diethoxyacetate with magnesium benzyl iodide. Much dibenzyl is formed simultaneously:



With the exception of isopropylglyoxal and benzylglyoxal, which are white, crystalline solids, all the glyoxals which we have prepared are yellowish green liquids of characteristic odour. They may be distilled under diminished pressure without marked decomposition and the vapours resemble chlorine in colour. All the glyoxals dissolve in organic solvents with the production of an intense yellowish green solution. They reduce ammoniacal silver solutions in the cold and Fehling's solution on warming. On treatment with sodium hydroxide they yield the corresponding hydroxy acids whilst the enzyme "glyoxalase," which we have found in many animal tissues, brings about a similar reaction except that the resulting hydroxy acids are optically active:



and that the glyoxal then unites with nitrophenylhydrazine, but it is perhaps more plausible to assume that the first product of the reaction is an unsaturated acid obtained in very low concentration by keto-enolic tautomeric change:



EXPERIMENTAL.



Ethyl diethoxyacetacetate (86 grams; 1 mol.), sodium (34 grams; 3 mols.), and ethyl acetate (130 grams; 3 mols.) were used for the condensation, which was carried out in an apparatus similar to that described by Wahl and Doll (*Bull. Soc. chim.*, 1913, [iv], **13**, 265). To the ethyl diethoxyacetacetate heated to 85–90°, portions of 2 grams of sodium wire and 9 c.c. of ethyl acetate were added at half-hour intervals. The reaction was quite vigorous at first, but subsided toward the end, when the sodium and ethyl acetate could be added a little more rapidly. The seventeen additions of these substances should be made in about six hours. The liquid, which became dark brown and very viscous, was stirred continuously during the experiment. The reaction was allowed to proceed for four hours after the last addition of sodium and ethyl acetate, when there was still a small amount of sodium undissolved. Alcohol (30 c.c.) was added to dissolve the sodium residue, and then the oil, cooled somewhat but not allowed to become too viscous, was poured into a mixture of 130 c.c. of concentrated hydrochloric acid and 130 grams of ice. The oily layer was immediately separated, and the aqueous layer extracted once with a small quantity of ether. The oil and ethereal extract were mixed, and shaken with sodium carbonate solution until the aqueous layer was distinctly alkaline. The supernatant oil was then removed, the aqueous layer extracted once with ether, and the combined oil and ethereal extract were dried. The dark red oil was then subjected to fractional distillation. As soon as ether, alcohol, etc., had ceased to distil over, the operation was conducted under diminished pressure, and a fraction boiling mainly at 75–78°/7–8 mm. was obtained (bath at 100°). This fraction consisted mainly of unchanged ethyl diethoxyacetacetate and ethyl acetoacetate. The temperature of the bath was raised gradually to 135°, and a main fraction passed over, the thermometer rising rapidly to 112° and then slowly to 115°. This fraction (52 grams) consisted of ethyl γ -diethoxyacetacetate.

In order to obtain a high yield of this ester it is essential that the reaction and distillation should be carried out in one day. On account of the short time which can be allowed for drying the esters before distillation, the ethyl acetoacetate fraction contains a considerable amount of water, and a little is apt to pass over with the first portion of the main fraction, which should be collected separately. On refractionating the ethyl acetoacetate fraction with the bath heated to 75–80°, the distillate passed over at 60–65°/

6–8 mm., and about 5 c.c. of a liquid of higher boiling point remained in the distilling flask. The dry first portion of the main fraction was then added to this residue, and the bath heated to 105°. A few drops of liquid passed over at 60–70°/4–6 mm., and were added to the ethyl acetoacetate fraction. The bath was then heated to 130°, and the temperature of the distillate rose rapidly to 112°/4–6 mm., and remained constant. This distillate was mixed with the main fraction. The final yields thus obtained were 32 grams of the ethyl acetoacetate fraction and 76 grams of ethyl γ -diethoxyacetoacetate.

0.2116 gave 0.4263 CO₂ and 0.1556 H₂O. C=54.94; H=8.17.

C₁₀H₁₄O₃ requires C=55.04; H=8.25 per cent.

Ethyl γ -diethoxyacetoacetate is a colourless, highly refractive liquid, having an odour resembling that of ethyl acetoacetate, but somewhat sweeter. It gives a typical colour reaction with alcoholic ferric chloride solution.

Hydrolysis of Ethyl γ -Diethoxyacetoacetate: Methylglyoxalacetal
CH₃CO·CH(OEt)₂

Ethyl γ -diethoxyacetoacetate (6.5 grams) was shaken with *N*-potassium hydroxide (34 c.c.), when the ester slowly dissolved the solution turning slightly yellow. The liquid was boiled under reflux for fifteen minutes, when a colourless oil separated. This was extracted three times with ether, the ethereal solution dried, and distilled. After the ether had been removed the residual liquid was distilled under diminished pressure. The first fraction, boiling at 58–65°/24–30 mm. (bath at 100°), consisted of methylglyoxal acetal (3 grams). The second fraction distilling at 90–103°/2–4 mm. (bath heated from 100° to 160°) was unchanged ester (1.5 grams).

The methylglyoxalacetal thus obtained was identical in properties with that described by Wohl and Lange, and on hydrolysis with *N*/10 sulphuric acid behaved in typical fashion, giving a solution of methylglyoxal, which was identified by means of the bisnitrophenylhydrazone, which melted and decomposed at 300–302°, and gave the characteristic colour reaction with alcoholic sodium hydroxide solution (*J. Biol. Chem.*, 1913, **15**, 132).

Ethyl γ -Diethoxy- α -methylacetoacetate,
CH(OEt)₂CO·CHMe·CO₂Et.

A solution of sodium (4.4 grams; 1 mol.) in 50 c.c. of alcohol was added to ethyl γ -diethoxyacetoacetate (41.6 grams; 1 mol.) and a mixture of this and methyl iodide (30 grams) was heated

gently on the water-bath for half-an-hour, when it was neutral to litmus. Alcohol was then distilled off, water added to the residual liquid, the oil which separated was removed, and the aqueous layer extracted four times with small quantities of ether. The combined oil and ethereal extracts were dried and fractionated. After the ether had been removed, the oil boiled at 110–112°/4–6 mm., the yield being 42 grams:

$\sigma 195$ gave 0·4146 CO₂ and 0·1536 H₂O. C = 56·95; H = 8·60.
C₈H₁₆O₃ requires C = 56·90; H = 8·62 per cent.

The ester so obtained is a colourless liquid having, when freshly distilled, a faint, garlic-like odour. On adding a drop of ferric chloride solution to an alcoholic solution of the ester only a very slight darkening takes place, the characteristic colour reaction of methyl γ -diethoxyacetoacetate having disappeared.

Hydrolysis of Ethyl γ -Diethoxy- α -methylacetoacetate: Ethylglyoxalacetal, C₂H₅CO-CH(OEt)₂.

A solution of ethyl γ -diethoxy- α -methylacetoacetate (15·5 grams; 1 mol.) in methyl alcohol (50 c.c.) was boiled with 2*N*-potassium hydroxide (50 c.c.; 1½ mols.) under reflux for half an hour, when a colourless oil separated. The liquid was diluted with water, and extracted six times with small quantities of ether. After distilling off the ether and methyl alcohol from the dried ethereal solution 7 grams of ethylglyoxalacetal boiling at 62–68°/10–12 mm. (bath at 85°) were obtained. A few grams of unchanged ester remained in the distilling flask:

$\sigma 2197$ gave 0·4834 CO₂ and 0·1981 H₂O. C = 60·0; H = 10·0.
C₈H₁₆O₃ requires C = 60·0; H = 10·0 per cent.

This acetal is a colourless liquid with a pleasant, fruity odour.

Hydrolysis of Ethylglyoxalacetal: Ethylglyoxal, C₂H₅CO-CHO.

Ethylglyoxalacetal (4·5 grams) was boiled for one and a half hours with sulphuric acid (50 c.c. of 2 per cent. by volume) under reflux. The acetal behaved like that of methylglyoxal, the liquid becoming milky on warming and then clearing again on boiling. Till the oil passed into solution, and on distillation ethylglyoxal passed over readily with the steam, and separated from the first portion of the distillate as a yellow oil, which dissolved easily in ether.

With an aqueous solution of semicarbazide hydrochloride, ethylglyoxal gives a monosemicarbazone, C₆H₈O₂N₃, which crystallises from water, and melts and decomposes at 235–236°.

Ethyl γ -Diethoxy- α -dimethylacetacetate,
 $\text{CH}(\text{OEt})_2\text{CO}\cdot\text{CMe}_2\text{CO}_2\text{Et}$.

A solution of sodium (2·3 grams: 1 mol.) in 35 c.c. of alcohol was added to ethyl γ -diethoxyacetacetate (1 mol.), and a mixture of this and methyl iodide (slight excess over 1 mol.) was gently boiled on the water-bath for half-an-hour, when it was neutral to litmus. A second addition of 2·3 grams of sodium in 35 c.c. of alcohol and 18 grams of methyl iodide was then made, and after boiling for a further half hour the reaction was complete. The alcohol was distilled off, and water was added to the residue, which was then extracted with five small quantities of ether. The ethereal solution was dried and evaporated, and then *ethyl γ -diethoxy- α -dimethylacetacetate* (19 grams) distilled at 104–105°/4–6 mm. (bath at 115–120°):

0·2313 gave 0·4955 CO_2 and 0·1863 H_2O . C=58·42; H=8·95.
 $\text{C}_{12}\text{H}_{22}\text{O}_3$ requires C=58·54; H=8·94 per cent.

The ester is a colourless liquid, having, when freshly distilled, a faint, garlic-like odour. It gives no colour reaction in alcohol solution with ferric chloride.

Hydrolysis of Ethyl γ -Diethoxy- α -dimethylacetacetate:
isoPropylglyoxalacetal, $\text{CHMe}_2\text{CO}\cdot\text{CH}(\text{OEt})_2$.

A solution of ethyl γ -diethoxy- α -dimethylacetacetate (12 grams: 1 mol.) in methyl alcohol (27 c.c.) was boiled with 2*N*-potassium hydroxide (27 c.c.: 1·1 mol.) under reflux for half-an-hour. Water was then added, and the liquid was extracted five times with small quantities of ether. After distilling off the ether and methyl alcohol from the dried ethereal solution, 7 grams of *isoPropylglyoxalacetal*, boiling at 75–77°/10–12 mm. (bath at 100°), were obtained, about 1 gram of unchanged ester remained in the distilling flask.

The acetal is a colourless liquid possessing a pleasant, faint odour with a suggestion of peppermint.

Hydrolysis of isoPropylglyoxalacetal: isoPropylglyoxal,
 $\text{CHMe}_2\text{CO}\cdot\text{CHO}$.

Three grams of *isoPropylglyoxalacetal* were boiled for two hours under reflux with 10 c.c. of sulphuric acid (0·2 per cent. by volume). At the end of this time only a trace of oil was left. On distillation in a current of steam *isopropylglyoxal* (m. p. 95–96°), identical with the substance described by Conrad and Ruppert (*Ber.*, 197, 30, 882), was obtained. The *bis-p-nitrophenylhydrazone*, $\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_6$, crystallises from a mixture of nitrobenzene and toluene.

in glistening, scarlet prisms, melting and decomposing at 295°. The *α,β-dimethylcarbonyl*, $C_6H_{11}O_2N_3$, crystallises from water in masses of very pale yellow prisms, melting at 158–159°.

It was interesting to note that the specimen of crystalline *α-propylglyoxal*, which had been dried over sulphuric acid and kept in a well-corked specimen tube, after a few days had become liquid, and developed an intense, pungent odour. The change is probably connected with some process of polymerisation.

Ethyl γ-Diethoxy-α-methyl-α ethylacetooacetate,
 $CH(OEt)_2CO-CMeEt-CO_2Et.$

A mixture of ethyl *γ-diethoxy-α-methylacetooacetate* (20 grams: 1 mol.) and a solution of sodium (2 grams: 1 mol.) in alcohol (30 c.c.) was boiled gently on the water-bath for two hours with methyl iodide (1·2 mols.), when the reaction was complete. Ethyl alcohol was removed as far as possible on the water-bath, water added to the residue, and the oil which separated was removed, the aqueous layer being extracted three times with ether. The mixed oil and ethereal extracts were dried and distilled. After removal of the ether, *ethyl γ-diethoxy-α-methyl α ethylacetooacetate* (19·5 grams) distilled at 117–118°/3·5 mm. (bath at 130°):

•2166 gave 0·4756 CO₂ and 0·1778 H₂O. C 59·87; H 9·13.
 $C_{18}H_{24}O_4$ requires C 59·99; H 9·23 per cent.

The ester is a colourless, highly refractive liquid with a pleasant, fruity odour. It gives no colour reaction in alcoholic solution with ferric chloride.

Hydrolysis of Ethyl γ-Diethoxy-α-methyl α ethylacetooacetate:
sec.-Butylglycolacetal, $CHMeEt-CO-CH(OEt)_2$.

A mixture of ethyl *γ-diethoxy-α-methyl α ethylacetooacetate* (16 grams) dissolved in methyl alcohol (46 c.c.) and 2*N*-potassium hydroxide (46 c.c.: 1·5 mols.) was boiled for forty-five minutes, then diluted with water, and extracted six times with ether. The dried ethereal solution was distilled, when *sec.-butylglycolacetal* (8 grams), boiling at 82–83°/10 mm. (bath at 100°), was obtained, 1·1 gram of unchanged ester remained in the distilling flask:

•2316 gave 0·5426 CO₂ and 0·2237 H₂O. C 63·90; H 10·72.
 $C_{10}H_{20}O_3$ requires C 63·83; H 10·64 per cent.

The acetal is a colourless liquid having a pleasant odour suggestive of acetone.

Hydrolysis of sec.-Butylglyoxalacetal: sec.-Butylglyoxal,
 $\text{CHMeEt}\cdot\text{CO}\cdot\text{CHO}$.

The acetal (4.5 grams) was boiled under reflux with sulphuric acid (45 c.c. of 2 per cent. by volume) for five hours. On distillation in a current of steam a yellowish-green oil, fairly readily soluble in water, passed over, which possessed the characteristic caramel odour of glyoxals.

The free glyoxal gives a *monosemicarbazone*, $\text{C}_7\text{H}_{13}\text{O}_2\text{N}_3$, a waxy solid, which is much more soluble in water than the corresponding compounds of other glyoxals. The *bis-p-nitrophenylhydrazone* was prepared by boiling a solution of the glyoxal with *p*-nitrophenylhydrazine sulphate. After recrystallisation from a mixture of nitrobenzene and toluene it melted and decomposed at 275–276°.

0.1089 gave 0.0238 N. N = 21.85.

$\text{C}_{14}\text{H}_{20}\text{O}_4\text{N}_2$ requires N = 21.88 per cent.

The *bis-p-nitrophenylhydrazone* crystallises in scarlet prisms and gives the characteristic blue solution in alcoholic sodium hydroxide solution.

Ethyl γ -Diethoxy-isopropylacetooacetate,
 $\text{CH}(\text{OEt})_2\cdot\text{CO}\cdot\text{CHPr}^2\cdot\text{CO}_2\text{Et}$.

Preliminary experiments in which it was attempted to introduce the isopropyl group by boiling an alcoholic solution of ethyl γ -ethoxyacetooacetate with isopropyl iodide in the presence of sodium ethoxide under reflux were unsatisfactory. The reaction took place much better in a sealed tube.

A mixture of ethyl γ -diethoxyacetooacetate (20 grams; 1 mol.) and sodium (21 grams; 1 mol.) dissolved in alcohol (25 c.c.), and isopropyl iodide (22 grams; 1.4 mols.) was heated in a sealed tube in a boiling water bath for eight hours. The product was then neutral to litmus. The alcohol was distilled off, the oil diluted with water, and extracted three times with ether. The dried ether solution was distilled, and after removing alcohol and ether, a fraction (15 grams) was obtained, which boiled at 112–116°/4–5 mm. (bath at 125–130°).

0.2190 gave 0.4786 CO_2 and 0.1799 H_2O . C = 59.6; H = 9.13.

$\text{C}_{15}\text{H}_{24}\text{O}_5$ requires C = 59.99; H = 9.23 per cent.

Ethyl γ -diethoxy-isopropylacetooacetate is a colourless, pleasant-smelling liquid, resembling the other esters of this series.

Hydrolysis of Ethyl γ -Diethoxy- α -isopropylacetooacetate:
isoButylglyoxalacetal, $\text{CHMe}_2\text{CH}_2\text{CO-CH(OEt)}_2$.

A mixture of ethyl γ -diethoxy- α -isopropylacetooacetate (15 grams; 1 mol.), dissolved in methyl alcohol (37 c.c.), and 2*N* potassium hydroxide (38 c.c.; 1.3 mols.) was boiled under reflux for one hour. The liquid was then diluted with water and extracted five times with ether. The dried ethereal solution was distilled, when isoButylglyoxalacetal (6.5 grams) boiling at 77–80°/10–12 mm. (bath at 100°) was obtained:

$\eta_{D}^{20.0}$ gave 0.4813 CO_2 and 0.1912 H_2O . C 63.72; H 10.31.

$\text{C}_9\text{H}_{16}\text{O}_5$ requires C 63.83; H 10.64 per cent.

On hydrolysis the acetal yielded isoButylglyoxal (*J. Biol. Chem.*, *18*, 38).

Ethyl γ -Diethoxy- α -benzylacetooacetate,
 $\text{CH(OEt)}_2\text{CO-CH(C}_6\text{H}_5\text{)}\text{CO}_2\text{Et}$.

A mixture of ethyl γ -diethoxyacetooacetate (7.4 grams; 1 mol.), ethanol (9.8 gram; 1 mol.) in 15 c.c. of ethanol, and benzyl chloride (5 grams; 1.3 mols.) was boiled under reflux for four and a half hours. The liquid was then neutral to litmus. The alcohol was distilled off, and water was added to dissolve the sodium chloride formed. An oil heavier than water separated, which was extracted three times with ether, and the dried ethereal solution distilled under 4–5 mm. pressure (bath at 100°). There remained in the flask 11 grams of a pale yellow oil, which was mainly ethyl γ -diethoxy- α -benzylacetooacetate. It was not distilled because previous attempts had resulted in decomposition.

The ester gives a port-wine coloration in alcoholic solution with ferric chloride.

Hydrolysis of Ethyl γ -Diethoxy- α -benzylacetooacetate:
Phenylethylglyoxalacetal, $\text{CH}_2\text{Ph-CH}_2\text{CO-CH(OEt)}_2$.

A mixture of the ester (11 grams; 1 mol.), dissolved in methyl alcohol (21 c.c.), and 2*N* potassium hydroxide (21 c.c.; 1.3 mols.) was boiled under reflux for two hours. The liquid was then diluted with water and extracted five times with ether. The dried ethereal solution was distilled, when phenylethylglyoxalacetal (6.5 grams) boiled over at 135–137°/3–5 mm. (bath at 160–170°).

Hydrolysis of Phenylethylglyoxalacetal: Phenylethylglyoxal,
 $\text{CH}_2\text{Ph-CH}_2\text{CO-CHO}$.

The acetal (5.5 grams) was boiled under reflux with sulphuric acid (30 c.c. of 2 per cent. by volume), and the product was

extracted four times with ether, the dried ethereal solution being distilled, when *phenylethylglyoxal*, boiling at $99-102^\circ/3-5$ mm. (bath at $130-140^\circ$), was obtained. The vapours were yellow, and condensed to a viscid, oily, intensely yellow liquid, having a sweet odour. It is only sparingly soluble in water, and not very readily volatile in steam. On keeping, the colour becomes less intense, and the liquid very much more viscous, due possibly to polymerisation.

The *bis-p-nitrophenylhydrazone*, $C_{16}H_{14}O_4N_6$, is best prepared by dissolving *p*-nitrophenylhydrazine in alcohol, adding the glyoxal and warming the solution. On keeping, the *bis-p*-nitrophenylhydrazone is slowly deposited in a pure condition from the solution. It crystallises in scarlet needles from a mixture of nitrobenzene and toluene, and melts and decomposes at 269° .

The constitution of phenylethylglyoxal was confirmed by converting it into α -hydroxy γ -phenylbutyric acid by the action of dilute alkali. About 1 gram of phenylethylglyoxal was boiled with 30 c.c. of *N* sodium hydroxide solution for fifteen minutes. The product was filtered to remove the oily scum, acidified, and extracted with ether. Crystalline α -hydroxy- γ -phenylbutyric acid was obtained which, on recrystallisation from a mixture of ether and light petroleum, melted at $104-105^\circ$.

THE HERTZ LABORATORY,
NEW YORK CITY.

NUTRITION RESEARCH LABORATORY
THE UNIVERSITY, LEEDS.

CXXXX. *Studies in Phototropy and Thermotropy*
Part V. Polymorphic 4-Hydroxybenzylidenearylamines Produced by Trituration and by the Influence of Sunlight.

By ALFRED SENIER AND ROBERT BENJAMIN FORSTER.

THAT 4-hydroxybenzylidenearylamines yield dimorphic varieties when triturated, which are distinguished by the triturated variety being deeper in colour than the original base, was shown in the case of two of these anils by Senier and Shepheard (T., 1909, 95, 197; 1954). It is now found that this character is common to all, which contain hydroxyl, in the *p*-position in the benzylidene group, and further that the change is not only indicated by a deepening of colour, but in some cases by a notable difference of melting point and also by quite different thermotropic behaviour. In one instant the change of colour produced by trituration is not from a pale

to a deeper colour, but the opposite, from red to orange. The deeper-coloured dimorphic variety is fairly stable, but on long keeping it very slowly returns to the original form, the latter change being accelerated by the absence of sunlight.

That trituration or rubbing is capable of producing polymorphic change, and is, indeed, an important means, generally, of bringing about chemical reactions, is well known. The paper recently communicated by Parker (this vol., p. 1504) not only adds to our knowledge of the subject to an important degree, but contains a useful list of references to previous work. Hitherto, however, no organic compounds and their reactions have been chiefly studied.

It is interesting to trace the analogy between the organic bases, which we have examined, and the well-known trituration dimorphism of mercuric iodide. For comparison, take the base 4 hydroxy benzylidene-*m*-chloroaniline. Yellow mercuric iodide between the ordinary temperature and a temperature of 126° is changed by trituration into the red, dimorphic variety; in like manner our base changes between the ordinary temperature and 110° from pale yellow to a deep yellow dimorphic variety. Both at a higher temperature, respectively above 126° and 110°, revert to their original paler modifications.

Continuing the main object of this inquiry, both dimorphic varieties have been examined, for phototropy and thermotropy between "the lower temperature" (that of solid carbon dioxide) and "the higher temperature" (a temperature just below the melting point of the substance). Thus we were able to study the phenomena of phototropy and thermotropy which depends on the formation and decomposition, as we think, of solid molecular aggregates (Senier and Shephard, T., 1909, 95, 1944) in the case of each of the two varieties which depend on polymorphism.

In the case of thermotropy, the higher limits of temperature above which it does not occur are noted.

It is well known that prolonged influence of sunlight produces changes in these solids generally not of a phototropic or reversible nature, but with the formation of non-reversible, and as regards sunlight, permanent polymorphic varieties. Many of the amines described exhibit this property.

Photoluminescence was sought for in all cases, but none was detected.

The following 4-hydroxybenzylideneamines were examined, and were prepared easily by bringing together equimolecular proportions of the respective aldehydes and arylamine bases in solution. They all dissolve more or less readily in the usual organic solvents.

4-Hydroxybenzylideneaniline, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}=\text{N}\cdot\text{C}_6\text{H}_5$, was described by Herzfeld (*Ber.*, 1877, **10**, 1271), who found it to melt at 191–192°. It crystallises from alcohol in pale yellow plates, and our specimen melts at 194–195° (corr.). It is dimorphous. Trituration changes it into a deeper-coloured dimorphic variety, which, however, on long keeping changes slowly back to the original compound, most readily when kept in the dark. The *paler-coloured variety* is thermotropic, becoming paler at "the lower temperature," and returning to the original colour at the ordinary temperature. The higher limit of thermotropy is about 160°. It is not changed by sunlight. The *deeper-coloured variety* is not phototropic, but on prolonged exposure to sunlight it changes to a brown, polymorphic form. It is thermotropic between the ordinary temperature and "the lower temperature." Above this, at about 110°, it becomes paler and returns to the original form.

4-Hydroxybenzylidene-*o*-toluidine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}=\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$

4-Hydroxybenzylidene-*o*-toluidine was first prepared by Mancini and Furlong (*Ber.*, 1909, **42**, 4389), who found it to melt at 160°. It crystallises from alcohol in brilliant, colourless prisms. Our specimen examined melts at 171–172° (corr.).

By trituration a greenish-yellow, *dimorphic variety* is obtained, which on long keeping reverts to the original compound. The *colourless variety* is not affected by sunlight. Above the ordinary temperature it becomes yellow, the thermotropic limit being about 150°. The *deeper-coloured variety* is not phototropic, but on prolonged exposure to sunlight changes to a brown, polymorphic form. It is thermotropic between the ordinary temperature and "the lower temperature," when it becomes colourless. At about 130° it loses its colour, and appears to be converted into the original compound.

4-Hydroxybenzylidene-*m*-toluidine was first prepared by Scott and Sheppard (T., 1909, **95**, 1951), who studied its thermal properties and also observed the dimorphic variety obtained by trituration. We have noted, further, that the thermotropic limit of temperature of the *paler-coloured variety* lies between 160° and 180°, and also that when the temperature of the *deeper-coloured variety* is raised to about 120° it becomes of the same colour as that in which the *paler-coloured variety* assumes at the same temperature and with which it appears to be identical. Neither variety is affected by sunlight.

4-Hydroxybenzylidene-*p*-toluidine was first described by Herzfeld (*Ber.*, 1877, **10**, 2196), who found the melting point to be 115°.

Our specimen, when crystallised from alcohol, consisted of pale yellow plates, which melted at 218° (corr.).

By trituration a deeper yellow *dimerophic variety* is produced, which loses colour very slowly on long keeping. *The paler-coloured variety* is not phototropic, but exhibits thermotropy at "the lower temperature," when it is nearly colourless. The higher thermotropic limit of temperature is about 190°. *The deeper-coloured variety* is also not affected by sunlight, but is thermotropic between the ordinary temperature and "the lower temperature." At about 110° its colour approximates nearly to that of the original compound, if that be compared at the same temperature, into which it appears to be converted.

*4 Hydroxybenzylidene-*o*-xylylidone*, OH-C₆H₄-CH=N-C₆H₃Me₂.

*4 Hydroxybenzylidene-*o*-xylylidone* crystallises from amyl alcohol in pale yellow needles, melting at 211–211.5° (corr.):

• 1316 gave 6.9 c.c. N₂ at 11° and 769 mm. N = 6.37.

C₁₅H₁₂ON requires N = 6.22 per cent.

*4 Hydroxybenzylidene-*o*-xylylidone* is dimorphous. By trituration it changes to a deeper yellow variety, which loses colour rapidly on keeping, especially when removed from the influence of sunlight. *The paler-coloured variety* is not phototropic, but exhibits thermotropy at "the lower temperature." The higher limit of thermotropy lies between 160° and 180°. Its colour is not changed by sunlight. *The deeper-coloured variety* is not phototropic, but on prolonged exposure to sunlight it forms a much deeper-coloured *polymorphic form*. It is thermotropic between the ordinary temperature and "the lower temperature." At about 130° its colour approximates to that of the original compound (compared at the same temperature), with which it appears to be identical.

*4 Hydroxybenzylidene-*m*-xylylidone* crystallises from light petroleum in nearly colourless plates, melting at 162–163° (corr.).

• 1220 gave 11.5 c.c. N₂ at 11° and 762 mm. N = 6.53.

C₁₅H₁₂ON requires N = 6.22 per cent.

*4 Hydroxybenzylidene-*m*-xylylidone* is dimorphous. By trituration it changes to a straw coloured variety, which loses colour on keeping, especially in the absence of sunlight. *The paler-coloured variety* is not phototropic, but exhibits thermotropy, its colour changing to yellow at about 140°, the higher thermotropic limit. *The deeper-coloured variety* exhibits phototropy at "the lower temperature." It is thermotropic between the ordinary temperature and "the lower temperature." Between 110° and 120° it appears to change into the paler-coloured variety.

Both these varieties behave in an exceptional manner when subjected for a week or two, successively to the influence of sunlight and its absence; they both develop a lemon-yellow colour, and apparently they are both converted into the same substance. The substance undergoes no further change in sunlight, but when placed in the dark it assumes, not a paler colour, but a deep brown.

4-Hydroxybenzylidene-*p*-xylylidine crystallises from amyl alcohol; almost colourless prisms, melting at 193—194° (corr.):

0.2873 gave 11.9 c.c. N₂ at 11° and 763 mm. N = 6.25.

C₁₅H₁₄ON requires N = 6.22 per cent.

4-Hydroxybenzylidene-*m*-xylylidine is dimorphous. By trituration it changes to a bright yellow variety, which loses colour, and gradually assumes its original form, on keeping, especially if removed from the influence of sunlight. The *paler-coloured variety* is not phototropic, but exhibits thermotropy between "the lower temperature" and the ordinary temperature. When heated above 130°, it appears to be converted into "the deeper-coloured variety." The *deeper-coloured variety* is thermotropic between "the lower temperature" and about 170°.

When subjected successively to the influence of sunlight and its absence, both varieties behave in a similar manner to the dimorphic varieties of 4-hydroxybenzylidene-*m*-xylylidine.

4-Hydroxybenzylidenechloroaniline, OH·C₆H₄·CH=N·C₆H₄·C₆H₅

4-Hydroxybenzylidene-*o*-chloroaniline crystallises from toluene, pale cream coloured plates, melting at 171—171.5° (corr.):

0.1914 gave 9.6 c.c. N₂ at 12° and 762 mm. N = 6.02.

C₁₄H₁₃ONCl requires N = 6.05 per cent.

4-Hydroxybenzylidene-*o*-chloroaniline is dimorphous. By trituration it changes to a pale yellow variety, which rapidly loses its yellow colour, the change taking place more quickly when kept in the dark. The *paler-coloured variety* is not phototropic, but exhibits thermotropy at "the lower temperature." The higher limit of thermotropy lies between 120° and 140°. The *deeper-coloured variety* is thermotropic at "the lower temperature." Between 80° and 90° it appears to change into the paler coloured variety.

4-Hydroxybenzylidene-*m*-chloroaniline separates from light petroleum in pale yellow crystals melting at 181—182° (corr.):

0.1713 gave 8.9 c.c. N₂ at 12° and 764 mm. N = 6.25.

C₁₄H₁₃ONCl requires N = 6.05 per cent.

4-Hydroxybenzylidene-*m*-chloroaniline is dimorphous. By trituration a deeper-coloured variety is produced, which on keeping loses colour rapidly at first, and then very slowly, becoming almost colourless.

same colour as the original crystals. *The paler coloured variety* is not phototropic, but is thermotropic between "the lower temperature" and a temperature of about 170°. *The deeper coloured variety* exhibits thermotropy between "the lower temperature" and ordinary temperature. At about 110° it changes into the paler-coloured variety. Neither variety is affected by sunlight.

1 *Hydroxybenzylidene-p-chloroaniline* crystallises from benzene in pale yellow plates melting at 184°–185° (corr.).

6 1657 gave 8·7 c.c. N₂ at 13·5° and 757·5 mm. N = 6·23.

C₁₃H₁₀ONCl requires N = 6·05 per cent.

3 *Hydroxybenzylidene-p-chloroaniline* is dimorphous. By trituration it changes to a canary-yellow coloured variety, which melts at 193°–194° (corr.). This variety loses colour gradually on keeping, but its melting point is lowered only a few degrees. *The paler-coloured variety* is not phototropic, but becomes somewhat darker on prolonged exposure to sunlight. It is thermotropic between "the lower temperature" and about 170°. *The deeper coloured variety* exhibits thermotropy between "the lower temperature" and the ordinary temperature, and behaves thermotropically in the same manner as the paler variety between the temperatures of 110° and 150°. Its higher melting point, however, shows that it is a distinct variety.

1 *Hydroxybenzylidenechromoaniline*, OH·C₆H₄·CH=N·C₆H₄Br.

4 *Hydroxybenzylidene-o-bromoaniline* crystallises from toluene in almost colourless plates melting at 160°–167° (corr.):

6 1936 gave 8·5 c.c. N₂ at 11·5° and 731 mm. N = 5·06.

C₁₃H₁₀ONBr requires N = 5·08 per cent.

4 *Hydroxybenzylidene-o-bromoaniline* is dimorphous. By trituration it changes to a pale yellow variety, which on keeping in the absence of light gradually resumes the original colour. *The paler-coloured variety* is not acted on by sunlight, but is thermotropic between "the lower temperature" and about 130°. *The deeper-coloured variety* is thermotropic between "the lower temperature" and the ordinary temperature. At a temperature of about 110° it appears to be converted into the paler variety. If exposed to the influence of sunlight for a long period it gradually changes to a true polymorphic form.

3 *Hydroxybenzylidene-m-bromoaniline* crystallises from toluene as pale yellow prisms melting at 160°–161° (corr.):

6 1990 gave 9 c.c. N₂ at 11° and 741·5 mm. N = 5·30.

C₁₃H₁₀ONBr requires N = 5·08 per cent.

4 *Hydroxybenzylidene-n-bromoaniline* is dimorphous. By tritura-

tion it changes to a canary-yellow coloured variety, which melts at 172–173° (corr.). On keeping this variety behaves in an exceptional manner, rapidly losing its colour, and then very slowly regaining it, whilst throughout the melting point does not alter. *The paler-coloured variety* is not altered by prolonged exposure to sunlight. It is thermotropic between "the lower temperature" and the ordinary temperature. *The deeper-coloured variety* exhibits thermotropy between "the lower temperature" and the ordinary temperature. When heated above 100° it behaves differently from the paler-coloured variety.

4-Hydroxybenzylidene-p-bromoaniline crystallises from toluene pale yellow plates melting at 193–194° (corr.):

D 2056 gave 8.9 c.c. N₂ at 10° and 748 mm. N = 5.13.

C₁₃H₁₀ONBr requires N = 5.08 per cent.

4-Hydroxybenzylidene-p-bromoaniline is dimorphous. By trituration a deeper-coloured variety is obtained, which melts at 203–204° (corr.). Like the corresponding variety of the former compound, this variety becomes quickly paler, but regains its depth of colour on prolonged keeping. *The paler-coloured variety* is phototropic at "the lower temperature"; on prolonged exposure to sunlight at the ordinary temperature it becomes slightly deeper in shade. It is thermotropic between "the lower temperature" and about 150°. *The deeper-coloured variety* also exhibits phototropy at "the lower temperature." It is thermotropic at "the lower temperature," but behaves differently to the paler variety when heated to temperatures above 100°. A still deeper-coloured *p-morphin form* is produced by prolonged exposure to sunlight.

*4-Hydroxybenzylidene-*a*minobenzoic Acids,*
OH-C₆H₄CH(NH₂)C₆H₄CO₂H.

4-Hydroxybenzylidene-a-aminobenzoic acid has been prepared by Wolf (*Monatsh.*, 1910, **31**, 903), who describes yellow and red modifications. It crystallises from nitrobenzene in deep yellow needles. On recrystallising from alcohol a mixture of a red variety and the yellow variety was obtained, but the crystals were not examined separately. It melts at 226–227° (corr.).

By trituration it changes to a slightly deeper-coloured variety which loses colour on keeping, especially in the absence of sunlight, when it changes back to the original variety. *The paler-coloured variety* is not affected by sunlight. It is thermotropic between "the lower temperature" and about 200°. *The deeper-coloured variety* exhibits thermotropy between the ordinary temperature and "the lower temperature." It appears to change into the paler

coloured variety at about 140° . On prolonged exposure to sunlight it changes to a brownish-coloured polymorphic form.

4-Hydroxybenzylidene-m-aminobenzoic acid crystallises from nitrobenzene in orange, hexagonal plates, melting and decomposing at $138-239^{\circ}$ (corr.):

12990 gave 15 c.c. at 11° and 747 mm. N = 5.92.

$C_{14}H_{11}O_3N$ requires N = 5.81 per cent.

4-Hydroxybenzylidene-m-aminobenzoic acid is dimorphous. When crystallised from alcohol a mixture of red and orange crystals is obtained, but either variety, when recrystallised from methyl alcohol or xylene, yields only the red variety. This red-coloured variety is converted into the orange variety by trituration. The *red-coloured variety* is not thermotropic, but becomes *orange-coloured* at a temperature just below its melting point. The *orange variety* is not affected by sunlight. It is thermotropic between "the lower temperature" and 150° ; above this limit, when it is terra cotta coloured, it becomes red at about 215° , and finally just below its melting point reverts to its colour at the ordinary temperature—the orange colour of the dimorphous variety obtained by trituration of the original red compound.

4-Hydroxybenzylidene-p-aminobenzoic acid crystallises from nitrobenzene in deep brownish yellow needles. It begins to decompose at 220° , and melts at $229-230^{\circ}$ (corr.):

11562 gave 7.9 c.c. N_2 at 11° and 748.5 mm. N = 5.98.

$C_{14}H_{11}O_3N$ requires N = 5.81 per cent.

4-Hydroxybenzylidene-p-aminobenzoic acid is dimorphous. By trituration it changes to a slightly deeper coloured variety, which loses colour on keeping, more readily in the absence of sunlight, getting eventually to the original variety. The *paler coloured variety* is scarcely affected by sunlight. On prolonged exposure the colour deepens slightly. It is thermotropic between the ordinary temperature and "the lower temperature." The *deeper coloured variety* is thermotropic between the ordinary and "the lower temperature." At higher temperatures this variety changed back into a *paler coloured variety*. The colour changed to a browner, polymorphic form by prolonged exposure to sunlight.

4-Hydroxybenzylidene-anisidines, $OH \cdot C_6H_4 \cdot CH(N \cdot C_6H_4)OMe$.

4-Hydroxybenzylidene-o-anisidine crystallises in cream coloured rods from solution in xylene. It melts at $183-183.5^{\circ}$ (corr.):
13062 gave 16.6 c.c. N_2 at 10° and 742.5 mm. N = 6.39.

$C_{14}H_{13}O_3N$ requires N = 6.17 per cent.

4-Hydroxybenzylidene-o-anisidine is dimorphous. By trituration

it changes to a canary yellow variety, which becomes paler on keeping, especially when removed from the influence of sunlight, and is eventually converted into the original variety. The *paler-coloured variety* is not phototropic, but prolonged exposure to sunlight causes it to become slightly deeper in colour. It is thermotropic between "the lower temperature" and about 150°. The *deeper-coloured variety* is both phototropic and thermotropic between "the lower temperature," and is converted into the paler form at about 130°. By prolonged exposure to sunlight a deeper colour develops, probably indicating a *polymorphic form*.

4-Hydroxybenzylidene-m-anisidine crystallises in cream-coloured prisms from methyl alcohol. It melts at 193—193.5° (corr.)

0.2172 gave 11.3 c.c. N₂ at 11° and 758 mm. N = 6.23.

C₁₁H₁₃O₂N requires N = 6.17 per cent.

4-Hydroxybenzylidene-m-anisidine is dimorphous. By trituration it changes to a pale yellow variety, which loses colour on keeping, especially if removed from the influence of sunlight. The *paler-coloured variety* is only slightly altered on prolonged exposure to sunlight. It is thermotropic between "the lower temperature" and about 140°. The *deeper-coloured variety* is thermotropic between the ordinary and "the lower temperature." At higher temperatures it behaves differently from the paler variety. On prolonged exposure to sunlight a brownish-coloured *polymorphic form* results.

4-Hydroxybenzylidene-p-anisidine crystallises from xylene as bright yellow plates melting at 211—211.5° (corr.):

0.1482 gave 7.5 c.c. N₂ at 8° and 757 mm. N = 6.12.

C₁₁H₁₃O₂N requires N = 6.17 per cent.

4-Hydroxybenzylidene-p-anisidine is dimorphous. By trituration it is converted into a deeper coloured variety, which becomes paler on keeping if removed from the influence of sunlight. The *paler-coloured variety* is not affected by sunlight, but is thermotropic between "the lower temperature" and about 200°. The *deeper-coloured variety* is thermotropic between the ordinary and "the lower temperature," and appears to be converted into the *paler-coloured variety* at about 180°. Prolonged exposure to sunlight produces a brown-coloured *polymorphic form*.

4-Hydroxybenzylidene-naphthylamine, OH·C₆H₄·CH=N·C₁₀H₇

4-Hydroxybenzylidene-a-naphthylamine crystallises from xylene in buff-yellow plates, melting at 191—191.5° (corr.):

0.2048 gave 9.7 c.c. N₂ at 11° and 744.5 mm. N = 5.57.

C₁₇H₁₃ON requires N = 5.67 per cent.

4-Hydroxybenzylidene-a-naphthylamine is dimorphous. By trituration it is changed into a deeper-coloured variety, which on keeping, especially in the absence of sunlight, becomes paler, but on long keeping faintly brown. The *paler coloured variety* is not affected by sunlight, but is thermotropic between "the lower temperature" and about 170°. The *deeper-coloured variety* is both phototropic and thermotropic at "the lower temperature." At about 110° it reverts to the paler variety. A deeper brownish-coloured *polymorphic form* is produced by prolonged exposure to sunlight.

4-Hydroxybenzylidene-β-naphthylamine crystallises from alcohol as deep yellow plates melting at 231.5° (corr.)

n_D²⁰ 1.772 gave 8.5 c.c. N₂ at 11° and 748 mm. N = 5.67.

C₁₇H₁₅ON requires N = 5.67 per cent.

4-Hydroxybenzylidene-β-naphthylamine is not changed in colour by trituration. It is not phototropic, but exhibits thermotropy between "the lower temperature" and about 200°.

UNIVERSITY COLLEGE,
GALWAY.

VXXXI.—*Diphenyl-2(3;2';3'- and -3;4;3';4'-tetra-carboxylic Acids.*

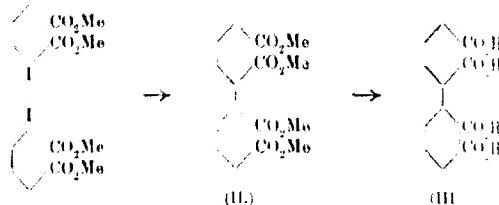
By JAMES KENNER and ANNIE MOORE MATHEWS.

In previous communications it has been shown that the case with such hydrindene derivatives may be prepared from those of cyclohexene finds its counterpart in the facility attendant on the formation of dibenzocycloheptadiene derivatives from those of *α,2-dimethylphenyl* (Kenner and Turner, T., 1911, **99**, 2101; Kenner, T., 1913, **103**, 615). It therefore seemed desirable to investigate the behaviour of some compound, such that, in any stage to which it might be submitted, the formation of a hydrindene derivative would be alternative to that of a dibenzocycloheptadiene derivative, and the most suitable compound for this purpose appeared to be *ωω'ω''ω'''-tetrabromo-2(3;2';3')-tetra-methylphenyl* (I):

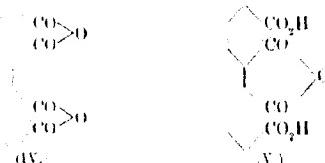


Whilst, however, the preparation of 2:3:2':3'-tetraphenyl diphenyl from 3-*iodo*-*o*-xylene would doubtless be easy to accomplish, it is evident from the account given by Cressley and R. of the preparation of 3-nitro-*xylene* (T., 1909, **85**, 215), that compound, and hence also the *iodo*-derivative, are only accessible with difficulty. It was therefore decided to investigate the behaviour of diphenyl 2:3:2':3'-tetracarboxylic acid, since diphenyl 2:3:2':3'-tetracarboxylic acid (ordinary diphenic acid) is well known to be convertible into an anhydride and an imide.

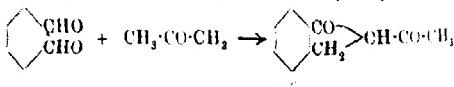
Tetramethyl diphenyl 2:3:2':3' tetra carboxylate (II) was obtained by heating *dimethyl 3 iodophthalate* with copper powder at 260°, and was converted into the *tetracarboxylic acid* (III) by hydrolysis in the usual manner:



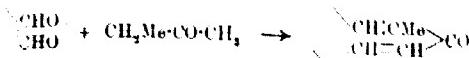
By treatment with dehydrating agents this acid was converted into the *dianhydride* (IV), and no sign of the monoanhydride could be detected:



Two possible explanations of the parallelism between the formation of hydridene and dibenzocycloheptadiene do, however, have been discussed (Kenner, T., 1913, **103**, 615), a notional preference being expressed for that one which is based on the suggestion that the strain in a *cycloheptadiene* ring is intermediate between that of the *cyclopentane* and *cyclohexane*. Further evidence in this direction may be derived from the work of Thiele and his collaborators (*Annalen*, 1906, **347**, 112; 1907, **352**, 287; 1910, **377**, 1). Whilst the condensation of phthalide with acetone results in the formation of 2-acetyl-3-hydridene,



erivatives of benzocycloheptadienone are produced when the α -one is replaced by its homologues. Thus, when methyl ethyl α -one is employed the reaction proceeds as follows:



Whatever influence determines the change in the course of the action is not sufficient to prevent the formation of the five-membered ring when, as in the following case, the production of a six-membered ring is rendered impossible:



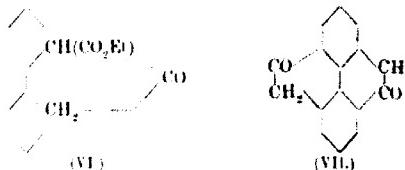
It is therefore difficult to escape the conclusion that the conclusion just referred to is justified. The anhydride formation stated above can also be interpreted as evidence in favour of a view that the cyclopentane ring is formed somewhat more easily than the cycloheptadiene ring; although it may be urged that considerations based on energetics that the formation of anhydride would in any case be more probable than that of a cyclic anhydride.

Recently, however, Kaufer's formula for diphenyl, on which a second explanation was based, has been upheld by Cain and Mckelwain (this vol., p. 1437), who prepared condensation products of benzidine with ortho-diketones, to which they assign the structure:



The present authors, however, regard it as somewhat disquieting that these and similar condensation products cannot be freed from decomposition from the two molecular proportions of the original compound which always accompany them, and the misgivings appear to have been entertained by Morgan and Mckelwain (T., 1908, **93**, 615). It may be observed that no such difficulties of this kind were encountered by Tauber in the preparation of similar condensation products from 2:2'diaminodiphenyl (T., 1902, **25**, 3287; 1893, **26**, 1703). Further, Cain and Mckelwain explain the isomerism of the two *o*-dinitrobenzidines by the supposition that the nitro groups occupy the 3:3' position in one compound, and the 3:5' position in the other, the steric hindrance of the nitro groups being assumed to prevent free rotation of the benzene nuclei. It would be anticipated that a

similar hindrance would be observed in the case of 2:2'-diphenylacetic acid. Such, however, is not the case. For, whilst diethyl diphenyldiacetate furnishes ethyl dibenzoycloheptadienone-*trans*-oxylate (VI) (Kenner, *loc. cit.*), diphenyldiacetyl chloride can be converted into dihydroxypyrene (VII) (Weitzenböck, *Mitt.*, 1913, **34**, 199).



It also appeared of interest to institute experiments on the esterification of diphenyl-2:3:2':3'-tetracarboxylic acid. It is well known that the benzene nucleus of certain naphthalene-*o*-anthracene derivatives, such as those represented by the formula:



exerts a strong hindrance on ester formation, but the effect of a phenyl group in the *ortho* position has not yet been studied. The considerations by which Petrenko-Krittschenko (*J. pr. Chem.*, 1900, [ii], **61**, 431, and later papers) has sought to explain the greater reactivity of cyclic ketones, as contrasted with their corresponding open-chain compounds, apply equally well in this case, and would lead one to expect the greater freedom for vibration of the phenyl group to confer on it a greater power of hindrance to esterification than that possessed by the benzene nucleus. And, indeed, it was found that diphenyltetracarboxylic acid (VIII), an acid of the type referred to, was converted only to a very small extent into the tetramethyl ester, when treated in the usual manner with methyl alcohol and sulphuric acid. When, however, the esterification was carried out in the presence of a considerable excess of sulphuric acid, a good yield of the tetra-methyl ester was obtained, an observation which agrees with the experience of Wegscheider (*Ber.*, 1895, **28**, 3128) in similar cases.

The weight of this evidence is also against Kauffler's formula. For it appears at least doubtful whether benzene nuclei in the relative positions assigned to them by him, would be capable of exerting such a hindrance.

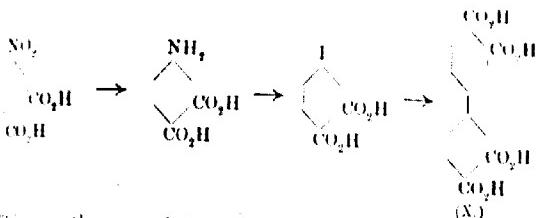
In our judgment, therefore, the most that can be said is that

under certain conditions diphenyl may assume the configuration suggested by Kaufler,⁴ just as the formation of cyclopropane indicates that one phase in the existence of the trimethylene dibromide molecule is represented by the formula IX:

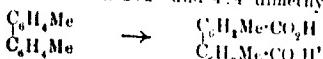


It does not, however, follow that such formulæ represent the actual condition of affairs.

During the preparation of the 3-nitrophthalic acid required for these experiments a considerable quantity of 4-nitrophthalic acid was obtained, and it was therefore decided to undertake the synthesis of diphenyl-3:4:3':4'-tetracarboxylic acid (X) in a manner similar to that adopted for the 2:3:2':3' tetracarboxylic acid, and presented in outline by the following scheme:



This was the more desirable since it had been found that the action of oxalyl chloride on 2:2' and 4:4' dimethyldiphenyl:



led to the production of unsymmetrical dimethyldiphenyldicarboxylic acids (Liebermann, *Ber.*, 1912, **45**, 1187; Kenner and Thom, T., 1913, **103**, 232). The behaviour of 3:3'dimethylphenyl was also studied by Liebermann and a symmetrical structure, that of a 3:3'dimethyldiphenyl 4:4'dicarboxylic acid, was assigned to the product, because on oxidation it was converted into tetracarboxylic acid:

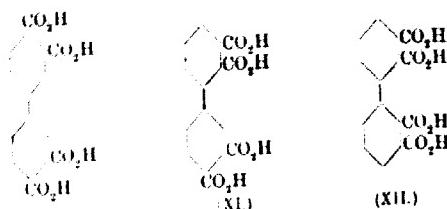


in which a dianhydride was obtained.

⁴ It had also been hoped to apply the reactions employed in the formation of compounds from 2':2'dimethyldiphenyl to the corresponding 3:3' and 4:4' derivatives (compare Kenner, *loc. cit.*, p. 618), but an intimation was received from Professor Finger of Darmstadt that he was engaged in the preparation of these substances for other purposes, and experiments in this direction were therefore desisted.

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It is, however, obvious that there are three formulae which are in agreement with this observation:



and the constitution of the acid in question had therefore not been decisively proved. The preparation of diphenyl-2:3:2':3'-tetracarboxylic acid disposed of formula XIII, but the unsymmetrical formula XI remained. It was found that, with the exception of minor points of divergence, the properties of Liebermann's compound agreed with those of the synthetical product, and the symmetrical structure was therefore confirmed.

The contrast thus brought to light between the behaviour of 2:2' and 4:4'dimethyldiphenyls on the one hand, and of 3:3'dimethyldiphenyl on the other, is only an apparent one. The substitution of diphenyl is known to take place in the 4:4' position, whilst methyl groups direct substituents into the ortho- and para-positions. In the case of 3:3'dimethyldiphenyl these two directive influences assist each other, but they are in opposition in the isomeric compounds, and the unsymmetrical substitution in these cases may be explained on the assumption that in one-half of the molecule the diphenyl directive influence asserts itself more strongly, whilst in the other half the influence of the methyl group prevails.

EXPERIMENTAL.

3-Nitrophthalic Acid.

Phthalic anhydride was nitrated according to the directions of Miller (*Jamalen*, 1881, **208**, 223). It was, however, found more convenient to subject the mixture of crude 3- and 4-nitrophthalic acids thus obtained to fractional crystallisation from water. In this manner 400 grams of pure 3-nitrophthalic acid were easily and rapidly obtained from 1600 grams of phthalic anhydride, and the mixture of acids contained in the mother liquors was then separated into its components in the manner indicated by Miller.

3-Aminophthalic Acid.

The preparation of this acid according to the directions given by Berndsen (*Ber.*, 1886, **19**, 160) was found to be an operation requiring considerable care, and the process finally adopted is therefore described in detail.

Zinc dust (15 grams) was added in small quantities to a mixture of nitrophthalic acid (25 grams) with 20 per cent. acetic acid (20 grams), the temperature of the mixture being maintained low 30°. If the operation had been successful a separation of crystals commenced when nearly all the zinc had been added. After eight hours the product, together with any unchanged zinc, is separated by filtration. The residue was then repeatedly extracted with small quantities (in all, 100 c.c.) of 20 per cent. concentrated sulphuric acid, when all the amino compound passed into solution, leaving some unchanged zinc. To the solution crystallised sodium acetate (150 grams) was then added. On stirring well the state passed into solution, and the double zinc acetate compound—the aminophthalic acid, together with sodium sulphate, was precipitated, and after a short time was collected for use in the subsequent operations.

3-Iodophthalic Acid.

The reduction product from the previous operation was dissolved in a warm mixture of 25 grams of concentrated sulphuric acid with 50 grams of water. The solution, after being cooled to 0°, was titrated; when near the end point it became converted into a ammonious yellow paste, and a concentrated solution of potassium iodide was then added. After some time the mixture was warmed until all the nitrogen had been evolved. Sulphurous acid having been added to remove excess of iodine, the iodophthalic acid, which precipitated out, was collected, washed, and dried at 100°.

Dimethyl 3 Iodophthalate.

Silver 3 iodophthalate (10 grams) was heated in a reflux apparatus on the water-bath with benzene (20 c.c.) and methyl iodide (5 grams). After three hours the ester was isolated in the usual manner, and purified by solution in light petroleum (b. p. 130°). In this way the ester was obtained in prisms melting 130°. When quite pure the ester is colourless, but readily assumes a pale yellow colour on exposure:

$\text{C}_{10}\text{H}_9\text{O}_4\text{I}$ gave 0.2831 AgI. $I = 39.20$.

$\text{C}_{10}\text{H}_9\text{O}_4\text{I}$ requires $I = 39.69$ per cent.

Vol. CV.

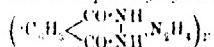
Tetramethyl Diphenyl-2:3:2':3'-tetracarboxylate (II).

Dimethyl 3-iodophthalate was heated in portions of 10 gms. to 240°, and in the course of twenty minutes an equal weight of copper powder was added in small quantities with continual stirring. The mixture was then heated at 260° for forty-five minutes, allowed to cool, and thoroughly extracted with chloroform; finally the solution was filtered, and concentrated to crystallisation. The ester was further purified by recrystallisation from benzene, from which it separated in prismatic needles melting at 167°.

The ester is sparingly soluble in cold alcohol, moderately so in hot alcohol, hot light petroleum (b. p. 90—120°) or benzene, and readily so in chloroform:

0.1522 gave 0.3190 CO₂ and 0.0640 H₂O. C=62.5; H=4.48
C₂₀H₁₄O₄ requires C=62.2; H=4.66 per cent.

Attempts to prepare a condensation product of the ester with ethyl acetate (compare Wislicenus and Kötzle, *Ber.*, 1877, 10 (1553) resulted in the formation of indefinite products, but when an alcoholic solution of the ester was digested with hydrating hydrate on the water bath for a considerable time, a yellow compound was gradually deposited. The product was readily soluble in water, and when the aqueous solution was acidified, a white precipitate, insoluble in all the solvents applied, was obtained together with a salt of hydrazine. Although the analytical figures were not sharp, there can be no doubt that the yellow compound was the *dihydrazone salt* of *diphenylhydrazine*,

*Diphenyl-2:3:2':3'-Tetracarboxylic Acid (III).*

The tetramethyl ester readily underwent hydrolysis when treated with alcoholic potassium hydroxide in the usual manner. The potassium salt of the acid separated in plates, and was collected. By acidifying a concentrated solution of the salt in hot water the acid was liberated and separated in hexagonal plates as the solid cooled. Owing to its great solubility in water it is difficult this way to separate all the acid from inorganic salts, but attempts to prepare the acid by decomposition of its sparingly soluble salt with hydrogen sulphide were unsatisfactory. The acid melts at 205°, passing over into the anhydride:

0.1332 gave 0.2732 CO₂ and 0.0424 H₂O. C=55.94; H=3.24
0.2170 lost 0.0106 at 110°. H₂O=4.9.

$\text{C}_{18}\text{H}_{16}\text{O}_8\text{H}_2\text{O}$ requires C = 55.17; H = 3.45; H_2O = 5.1 per cent.
M.W. = 348.

After dehydration at 110° :

$\text{C}_{16}\text{H}_{16}\text{O}_8$ gave 0.2131 CO_2 and 0.0312 H_2O . C = 57.80; H = 3.41.
 $\text{C}_{16}\text{H}_{16}\text{O}_8$ requires C = 58.18; H = 3.03 per cent.

The *anhydride* (IV) was obtained in two ways, namely, (1) the tetra-carboxylic acid was heated in a reflux apparatus with twice its weight of acetyl chloride on the water bath, until hydrogen chloride was no longer evolved, and finally the excess of acetyl chloride was removed by evaporation.

(2) When 2:2'-carbomethoxydiphenyl 3:3' dicarboxylic acid was heated to a temperature just above its melting point, methyl alcohol was rapidly evolved, and the mass solidified.

The crude product in each case was purified by crystallisation in nitrobenzene, and separated in hexagonal plates, which melted 265° . The anhydride is stable towards cold sodium hydrogen carbonate solution, and is moderately soluble in nitrobenzene or acetone, but only sparingly so in acetone:

$\text{C}_{16}\text{H}_{16}\text{O}_6$ gave 0.3490 CO_2 and 0.0290 H_2O . C = 65.01; H = 2.2.
 $\text{C}_{16}\text{H}_{16}\text{O}_6$ requires C = 65.31; H = 2.04 per cent.

Partial Hydrolysis of Tetramethyl Diphenyl 2:3:2':3' tetra-carboxylate.

A solution of the tetramethyl ester in methyl alcohol was heated in a reflux apparatus on the water bath with the amount of potassium hydroxide solution theoretically requisite for the hydrolysis of two of its four carbomethoxy groups. After half an hour the solution was neutral, and was freed from methyl alcohol by evaporation. When the aqueous solution of the residue was titrated, a precipitate of 2:2'-carbomethoxydiphenyl 3:3' dicarboxylic acid was obtained. The acid crystallised from alcohol in long prisms, which melt at 205° with decomposition, and form part of the anhydride:

$\text{C}_{18}\text{H}_{16}\text{O}_8\text{C}_2\text{H}_6\text{O}$ required 9.5 c.c. N/10 NaOH. Equivalent 190.3.
 $\text{C}_{18}\text{H}_{16}\text{O}_8\text{C}_2\text{H}_6\text{O}$ requires M.W. = 404.

It was hoped to obtain the isomeric 3:3' dicarbomethoxydiphenyl dicarboxylic acid by esterification of the anhydride with the stated amount of sodium methoxide (compare the formation of 2:2-carbomethoxybenzoic acid from nitrophthalic anhydride, Schöder, *Mosch. J.*, 1900, **21**, 787), but experiment showed a mixture of esters was produced in this manner.

Esterification of Diphenyl-2:3:2':3'-tetracarboxylic Acid.

A solution of 3.67 grams of the acid in 20 c.c. of methyl alcohol was heated with 1 c.c. of concentrated sulphuric acid for six hours in a reflux apparatus. The product was poured into water, rendered alkaline with sodium carbonate solution, and extracted with ether. In this manner 0.09 gram of the tetramethyl ester (melting point, 162°) was obtained, and it is thus apparent that the esterification of the acid is not complete under ordinary conditions.

Diethyl 4 Iodophthalate.

This compound has previously been described by Edinger, who does not, however, give details of its preparation (*J. pr. Chem.*, 1896, [ii], 53, 375).

A solution of diethyl 4-aminophthalate (20 grams) in dilute sulphuric acid (300 c.c.) was decolorised by boiling with charcoal, filtered, cooled to 0°, and diazotised. A concentrated solution of potassium iodide was then added, and after standing the mixture was heated until the evolution of nitrogen was complete. The ethereal solution was washed successively with sodium carbonate and sodium thiosulphate solutions, dried, and distilled. In this manner the ester was obtained as a colourless liquid, boiling at 235–238°, and remarkable for the readiness with which it undergoes hydrolysis by alkali hydroxide.

Dimethyl 4 Iodophthalate.

It was anticipated that this compound would be better suited for the preparation of diphenyl-3:4:3':4'-tetracarboxylic acid than the diethyl ester. The latter was therefore hydrolysed by a 50 per cent. potassium hydroxide solution (30 grams) to a mixture of the ester (33 grams) with absolute alcohol (55 c.c.). Heat was evolved, and the mixture solidified almost immediately. The potassium salt thus formed was collected, and the acid eluted from it in the usual manner.

The acid was then esterified with methyl alcohol and concentrated sulphuric acid. The product, after pouring into water, was treated with dilute sodium carbonate solution, and worked up in the usual manner. It was found that the alkali extracted a considerable amount of acid ester, which was recovered and again sublimed.

esterification. In this manner the ester was obtained as a colourless oil, boiling at 219°:

• 1156 gave 0.2994 AgI. I = 39.81.

$C_{10}H_8O_4$ I requires I = 39.68 per cent.

Tetramethyl Diphenyl 3:4:3':4' tetra carboxylate.

The conversion of dimethyl 4-iodophthalate into the diphenyl derivative was carried out in the same manner as already described in the case of the 3-iodophthalic ester, the product being isolated by extraction with ether. The ester was accompanied by a considerable amount of oily matter, and crystallised from the ethereal solution in comparatively poor yield. It was purified by repeated crystallisation from methyl alcohol. According to Liebermann (*loc. cit.*), the melting point of his product was raised, in this way, from 91° to 99°. In the present case, however, it was observed that when two portions of the same sample were recrystallised, the one from a hot concentrated solution, the other from a cold dilute solution, the products melted at 101° and 93°. On one occasion a melting point of 106°, with softening at 91°, was observed. It is therefore apparent that two forms of ester exist (Found, C, 62.32; H, 4.04. $C_{20}H_{14}O_6$ requires C, 62.18; H, 4.66 per cent.).

Diphenyl 3:4:3':4' Tetra carboxylic Acid (X).

This acid was prepared by the hydrolysis of its tetramethyl ester in the usual manner, and was isolated by acidifying a somewhat dilute aqueous solution of its potassium salt. In this way it was once obtained in the pure condition. It was much less soluble in water than the 2:3:2':3' isomeride, and separated in needles, which contained 2 molecular proportions of water of crystallisation (Liebermann gives 1--1½):

• 1158 gave 0.3044 CO_2 and 0.0534 H_2O . C, 52.2; H, 3.73.

• 1159 lost 0.0428 H_2O at 115°. H_2O , 9.97.

• 1160 required 16.43 c.c. N/10 KOH. M.W., 365.

$H_2O_2 \cdot 2H_2O$ requires C, 52.46; H, 3.83; H_2O , 9.84 per cent. M.W., 366.

The dehydrated acid was also analysed:

• 1117 gave 0.3084 CO_2 and 0.0384 H_2O . C, 58.13; H, 2.94.

$C_{16}H_{16}O_8$ requires C, 58.18; H, 3.03 per cent.

Contrary to the statement of Liebermann, it was not found that X had undergone further dehydration, with the production of anhydride, when heated at 145°.

The anhydride was, however, prepared by heating the acid with excess of acetyl chloride until no further reaction took place. After crystallisation from nitrobenzene, it was obtained in needles, which melted at 292° (Found, C=64.8; H=2.29. $C_{10}H_8O_6$ requires C=65.31; H=2.04 per cent.).

In conclusion, the authors wish to express their gratitude to the Research Fund Committee of the Chemical Society for a grant which defrayed the cost of this investigation.

THE UNIVERSITY,
SHEFFIELD.

CCXXXII.—*The Absorption Spectra of the Vapours and Solutions of Various Derivatives of Benzaldehyde.*

By JOHN EDWARD PURVIS.

In previous communications (Purvis and McCleland, T., 1913, 103 1088, and Purvis, *ibid.*, 1638) the absorption spectra of benzaldehyde and some of its derivatives have been described. It is proved that the vapours of several of these derivatives show fewer absorption bands than benzaldehyde itself. In other instances no such bands were observed, and that the phenomena were then similar to the solution bands, the chief difference being one of position.

This author has continued the investigation with a number of other derivatives of benzaldehyde to see how far and in what directions various isomeric compounds and other compounds derived from benzaldehyde influence the type of absorption when they are in the vaporous condition and in alcoholic solution.

The substances examined were: *o*, *m*, and *p*-chlorobenzaldehydes, *o*, *m*, and *p*-tolualdehydes, *o*, *m*, and *p*-hydroxybenzaldehydes, anisaldehyde, *o*, *m*, and *p*-phthalaldehydes, cuminaldehyde, cinnamaldehyde, benzaloxime, benzylidene chloride, benzaldehyde with hydrogen sulphite, mandelonitrile, benzoyl chloride, and cyclohexanecarboxylic aldehyde.

The experimental methods have been described before. The deposed cadmium spark was used as the source of light. The absorption tube for the study of the vapours was usually exhausted and filled with nitrogen so as to eliminate as much as possible oxidation of the compounds. For the investigation of the solutions the substances were dissolved in alcohol.

o-chlorobenzaldehyde.—The alcoholic solution showed two bands (Fig. 1, I), which are not unlike those found in benzaldehyde (loc. cit.), except that they are shifted more towards the red and

The vapour of the substance in a 200 mm. tube at various temperatures and pressures showed the following phenomena. The abbreviations descriptive of the separate bands are those which have been used in previous communications:

	35°	45°	55°
774 mm.	825 nm.	844 nm.	860 nm.
The rays were transmitted to about $\lambda 2470$ when the following weak bands were observed.			
	λ	λ	
	2988 v.w.	3003 v.w.	
	2985 w.	2998 "	
	2992 w.	2995 w.	
	2989 w.	2993 w.	
	2986 mod.w.	2990 mod.w.	
	2979 v.w.	2986 mod.str.	
	2974 "	2979 v.w.	
	2968 "	2974 "	
	2962 "	2968 "	
	2958 "	2962 "	
	2954 mod.w.	2958 "	
	2950 "	2954 mod.w.	
	2944 v.w.	2950 "	
	2919 "	2954 w.	
	2906 "	2919 v.w.	
	2902 "	2906 "	
	2898 "	2902 "	
	2894 "	2898 "	
	2891 v.w.	2894 "	
	2883 w.	2891 v.w.	
		2883 w.	
20°			75
730 mm.			878 nm.
The rays were transmitted to Cd 2144.			
			The rays were absorbed from $\lambda 3050$ to about $\lambda 2600$ and then feebly transmitted to $\lambda 2570$.
20°			
730 mm.			
The rays were transmitted to about $\lambda 2470$ when the following weak bands were observed.			
	λ	λ	
	2468 v.w.	2800	
	2460 "	2800	
	2456 "	2800	
	2451	2800	
and then transmitted to Cd 2144.			
			From here the rays were absorbed from $\lambda 2780$ to $\lambda 2570$. The rays were absorbed from $\lambda 3050$ to about $\lambda 2600$ and then feebly transmitted to $\lambda 2570$.
25°			
808 mm.			
2992 v.w.			
2989 "			
2986 "			
These rays were then transmitted to $\lambda 2478$, and absorbed from here to $\lambda 2320$; they were then feebly transmitted to Cd 2144.			

The results show that there were a considerable number of bands

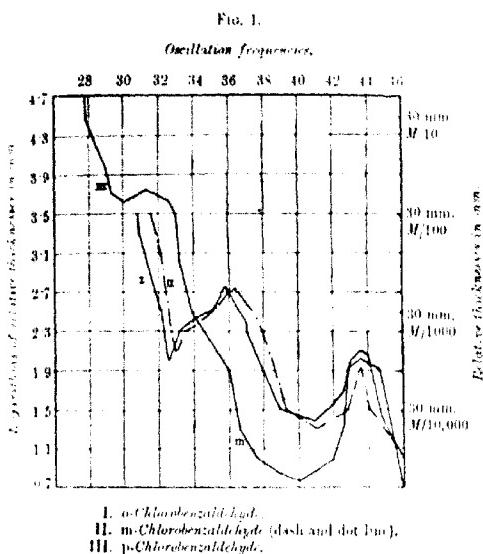
in the vapour which were absent in the solution; and that, on the other hand, as the temperature and pressure increased, the absorption of the vapour was comparable with that of the solution in so far as the disappearance of the vapour bands is concerned and the appearance of two wide large bands.

m-Chlorobenzaldehyde.—The alcoholic solution showed two bands (Fig. 1, II), which are not unlike the two bands of the ortho compound, but there is a slight difference in position. The vapour of the substance in a 200 mm. tube showed the following phenomena:

	18° 774 mm. λ	45° 844 mm. λ	55° 860 mm. λ	60° 874 mm. λ	
The rays were transmitted to about λ 2440 and then the following weak bands were observed.	2972 v.w. 2968 .. 2964 .. 2960 .. 2957 .. 2958 w. 2930 w. 2927 v.w. 2413 .. 2410 .. 2403 ..	2972 w. 2968 w. 2964 w. 2960 mod.str. 2957 .. 2951 .. 2949 mod.w. 2945 v.w. 2935 .. 2930 .. 2925 .. 2922 w.	2972 w. 2968 w. 2964 w. 2960 mod.str. 2957 .. 2951 w. 2949 mod.str. 2945 w. 2935 w. 2930 w. 2925 w. 2922 mod.w.	3013 v.w. 3007 .. 2972 mod.w. 2967 w. 2964 w. 2959 mod.w. 2957 .. 2952 mod.w. 2950 mod.w. 2946 .. 2935 .. 2930 .. 2924 .. 2922 mod.w.	3013 v.w. 3007 .. 2972 mod.w. 2967 w. 2964 w. 2959 mod.w. 2957 .. 2952 mod.w. 2950 mod.w. 2946 .. 2935 .. 2930 .. 2924 .. 2922 mod.w.
The rays were then transmitted to Cd 2144.	2915 w. 2912 .. 2904 v.w. 2901 .. 2892 .. 2886 .. 2876 w.	2915 w. 2912 mod.w. 2904 v.w. 2901 .. 2892 .. 2886 .. 2876 mod.w.	2915 w. 2912 mod.w. 2904 v.w. 2901 .. 2892 .. 2886 .. 2876 mod.w.	2916 w. 2913 mod.w. 2904 w. 2901 w. 2892 v.w. 2886 .. 2876 w.	2916 w. 2913 mod.w. 2904 w. 2901 w. 2892 v.w. 2886 .. 2876 w.
30° 818 mm.	2869 v.w. 2862 .. 2859 .. 2856 .. 2847 .. 2843 v.w.	2869 w. 2862 w. 2859 w. 2856 w. 2847 w. 2843 v.w.	2869 w. 2862 w. 2859 w. 2856 w. 2847 w. 2843 v.w.	2869 v.w. 2862 .. 2859 .. 2856 .. 2847 .. 2843 ..	2869 v.w. 2862 .. 2859 .. 2856 .. 2847 .. 2843 ..
The rays were transmitted to about λ 2440 and then the following bands were observed.	2438 w. 2430 v.w.	The rays were then transmitted to λ 2450.	The rays were then transmitted to about λ 2480.	The rays were then transmitted to λ 2500.	
The rays were then absorbed to Cd 2329 and then transmitted to Cd 2144.	2486 ..	75° 904 mm. λ	90° 934 mm. λ		
	3013 v.w. 3007 ..	3013 v.w. 3007 ..	The rays were absorbed between λ 2480 and λ 2600 and then transmitted to λ 2500.		
	The rays were then absorbed from λ 2980 to λ 2730 and then transmitted to λ 2500				

Again, in the meta-compound the vapour showed a considerable number of bands which were absent in the solution. The shift of the vapour bands towards the more refrangible end of the spectrum as compared with the vapour bands of the ortho compound is also noticeable.

p-Chlorobenzaldehyde.—The solution phenomena of the com-



pounds are markedly different from those of the ortho- and meta-compounds. It will be seen (Fig. 1, III) that the more refrangible band is much wider and stronger than the corresponding band of the ortho- and meta-compounds, and there is only a trace of the less refrangible one. There is also a greater shift in the position of the two bands and of the line of general absorption towards the red end. The vapour of the substance in a 200 mm. tube showed the following phenomena:

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15°	30°	55°	60°	
774 mm.	814 mm.	860 mm.	874 mm.	
The rays were transmitted to λ 2120.	The rays were feebly transmitted between λ 2330 and λ 2370, and then more strongly to λ Cd 2144.	λ 2865 w. 2858 w. 2853 w. 2847 w. 2838 v.w. 2834 .. 2831 .. 2828 .. 2825 .. 2822 .. 2817 .. 2813 .. 2811 .. 2808 .. 2805 .. 2795 .. 2788 .. 2781 .. 2754 w.	λ 2865 m.s. 2858 .. 2853 .. 2847 m.s. 2838 w. 2834 w. 2831 w. 2828 w. 2825 w. 2822 v.w. 2817 .. 2813 .. 2811 .. 2808 w. 2805 w. 2795 v.w. 2788 w. 2781 v.w. 2754 w.	
There were no traces of any weak refrangible bands like those found in the ortho- and meta-compounds in the more refrangible regions.				
45°				
844 mm.				
A 2865 v.w. 2858 .. 2853 w. 2847 mod.str.				
The rays were then transmitted to about λ 2550, and then absorbed to about λ 2300; after this they were transmitted to λ 2144.		The rays were then transmitted to λ 2570, and then absorbed to λ Cd 2144; λ 2144 was also visible.	The rays were then transmitted to λ 2144, after which there was complete absorption.	

75
904 mm.

A moderately wide band between λ 2865 and λ 2847, and also one between λ 2838 and λ 2825, that is, the bands of the two groups found at 55°, were widened into each other and formed two fairly wide bands at the higher temperature and pressure. The rays were then feebly transmitted to λ 2144.

90°
934 mm.
A

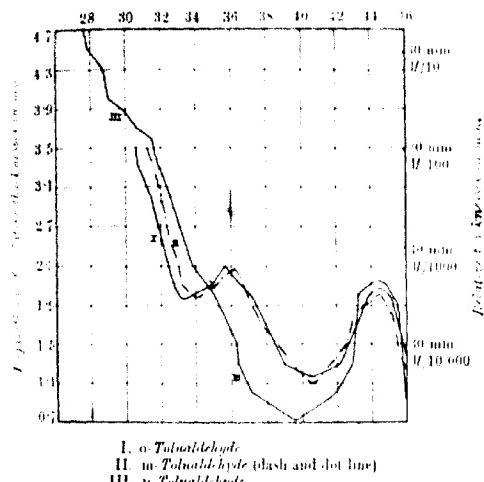
The rays were transmitted to λ 2900, after which there was complete absorption.

Again, in the para-compound the vapour showed a number of bands which were all absent in the solution. It is also to be noticed that there were no vapour bands on the less refrangible edges of the more refrangible band corresponding with the vapour bands found in this region in the ortho- and meta-compounds. These bands, ranging from λ 2438— λ 2403 in the meta-compound, were much weaker than the bands ranging from λ 2469— λ 2437 in the ortho-compound. In the earlier investigation of the vapour of benzaldehyde (*loc. cit.*) at 30° and 799 mm. there was a wide band in this region, in which there was no appearance of any fine bands.

The band ranged from $\lambda 2455$ — $\lambda 2160$. The vapour has been examined again at lower temperatures and 760 mm. pressure, and with a very small trace of the vapour in the tube to see if any weak bands had been missed. No such bands were observed, however, and the following notes describe the phenomena observed:

- A 18%. The rays were feebly absorbed between about $\lambda 2425$ and the Cd line 2329 and then transmitted to $\lambda 2120$.
- " 21%. The rays were feebly absorbed between $\lambda 2430$ and Cd 2265 and then transmitted to $\lambda 2125$.
- " 25%. The rays were absorbed between $\lambda 2440$ to Cd 2220 and then transmitted to $\lambda 2125$.

FIG. 2.

Oscillation frequencies.

- I. o-Tolualdehyde
- II. m-Tolualdehyde (dash and dot line)
- III. p-Tolualdehyde.

With regard to the general appearance of the vapour bands of the three isomerides, there appears to be some resemblance in the groups of bands the head of which in the ortho compound is at $\lambda 2956$, in the meta-compound at $\lambda 2957$, and in the para compound at $\lambda 2947$, although they differ in position. These stronger series of bands are not unlike the stronger bands of benzaldehyde at $\lambda 291$, $\lambda 2886$, $\lambda 2850$, and $\lambda 2840$ (*loc. cit.*). No exact comparison, however, can be made in these directions until it is assured that the radiant energy passes through the same number of mole-

molecules at the same temperature and pressure, and the experimental conditions of the vapours do not imply this.

It is also to be noticed that the number of vapour bands in the three isomerides is less than that found in the vapour of benzaldehyde.

o-Tolualdehyde.—The solution bands (Fig. 2, I) are not unlike those of *o*-chlorobenzaldehyde and of benzaldehyde.

The vapour of the substance in a 200 mm. tube showed the following phenomena:

	20°	35°	60°
	756 mm. A 2930—2922 w. 2804—2886 v.w.	802 mm. A 2974—2966 w. 2930—2919 mod.str. 2898—2885 w.	856 mm. The rays were absorbed between λ 2980 and λ 2630 and then transmitted to about λ 2110.
The rays were then transmitted to about λ 2450; from here they were absorbed to about λ 2340 and then transmitted to Cd 2144.		The rays were then fairly well absorbed between λ 2870 and λ 2776 and then transmitted to λ 2520.	
	45°	75°	
	780 mm. A 2974—2966 v.w. 2930—2918 mod.str. 2895—2884 v.w.	826 mm. A 2977—2960 mod.str. 2934—2917 " 2902—2883 "	886 mm. A The rays were absorbed from λ 2870 to λ 2764 and then transmitted to λ 2520.
The rays were then fully absorbed from the Cd line 2880 to about λ 2780 and then transmitted to about λ 2480; beyond this the rays between λ 2250 and λ 2144 were feebly visible.			

m-Tolualdehyde.—The solution bands (Fig. 2, II) are not unlike those of the ortho compound, but there is a slight difference in position.

The vapour of the substance showed the following phenomena:

	15°	25°	35°
	745 mm. A 2927—2918 w. 2914 w.	788 mm. A 2927—2920 mod.str. 2914 mod.w.	790 mm. A 2928—2918 mod.str. 2914 mod.str.
The rays were then transmitted to λ 2430 and then absorbed to Cd 2329, from where they were transmitted to λ 2144.		The rays were then transmitted to about λ 2470, then absorbed to Cd 2265, beyond which the Cd line 2144 was well marked.	The rays were then transmitted to λ 2785 and the Cd lines 2134 and 2144 were very strong. The rays showed a slight of weakening between λ 2875 and λ 2780.

	45°	60°	75°
	815 mm.	845 mm.	875 mm.
λ	λ	λ	The rays were absorbed from λ 2978; the Cd between λ 2960 and line 2573 was visible.
2925 - 2920 mod.str.		The rays were absorbed between λ 2960 and λ 2680, and thence transmitted to about 90°	
2914 mod.str.			
2890 v.w.			
2865 - 2890 v.w.			
	λ 2540.		905 mm.
The rays were fairly well absorbed between λ 2875 and 2573 and then transmitted to λ 2510.			
		The rays were absorbed from λ 2980.	

p-Tolualdehyde.—The solution curve (Fig. 2, III) is different from that of the ortho- and meta compounds. There is a doubtful trace of a less refrangible band as indicated by the rapid extension in the rays between $1/\lambda$ 2900 and $1/\lambda$ 3150 (λ 3445 - λ 3175), and the more refrangible band is much stronger and wider than the corresponding one of the other two isomerides. In this respect it is comparable with *p*-chlorobenzaldehyde.

The vapour of the substance showed the following phenomena:

	15°	35°	60°
	745 mm.	790 mm.	845 mm.
λ	λ	λ	λ
2843 v.w.	2846	2843 mod.str.	2855 - 2843 mod.str.
	2833 w.		
the rays were then transmitted to λ 2480 and absorbed between λ 2340 and λ 2340 and then transmitted to the Cd line 2144.	2817 w.		The rays were weak between λ 2810 and the Cd line 2748; then weakly transmitted to λ 2590.
25°	568 mm.	45°	55°
λ	λ	λ	905 mm.
2843 w.	815 mm.	λ	90°
the rays were then transmitted to λ 2500, absorbed to Cd 2329 and then transmitted to 2144.	2854 w.	2845 - 2843 mod.str.	The rays were absorbed from λ 2960.
		2833 w.	
		2817 w.	
The rays were then transmitted to λ 2560.			

The vapours of the three isomeric tolualdehydes do not show a number of bands like those described in the three isomeric chlorobenzaldehydes. There are only a few somewhat diffuse bands, and these disappear at the high temperatures, when two large bands appear not unlike the solution bands and differ from them only in position.

p-Chloraldehyde.—The solution curve shows two large bands (Fig. 3, I). The less refrangible one is much wider and stronger

than the less refrangible band of either benzaldehyde or of the halogen and methyl derivatives, and there is a greater shift toward the red end.

The vapour of the substance showed the following phenomena.

At the lower temperatures and pressures the vapours showed a number of well defined bands on the less refrangible edge of a large band on the more refrangible side. These bands were found in two different samples of salicylaldehyde which had been redistilled. The groups of bands *A*, *B*, *C*, and *D* are very similar in appearance, and the groups of bands beyond *D* show signs of division which are not sufficiently marked to measure the constituents. At the higher temperatures and pressures these bands disappear, and the two large bands are then comparable with the solution bands.

m-Hydroxybenzaldehyde.—The solution curve shows two bands (Fig. 3, II). They are comparable with those of the ortho compound, except that there is some difference in position.

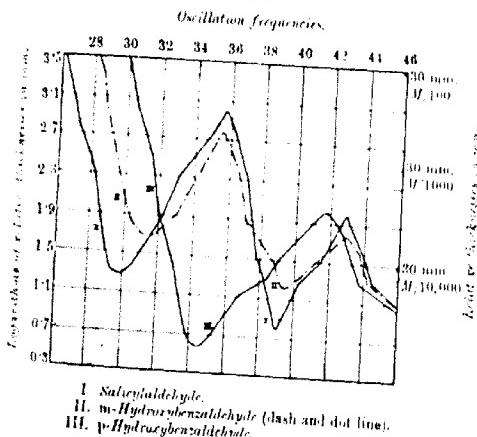
SOLUTIONS OF VARIOUS DERIVATIVES OF BENZALDEHYDE. 2491

The vapour of the substance showed the following phenomena:

88°	118°	158°
764 mm.	764 mm.	764 mm.
Rays absorbed between $\lambda 2462$ and $\lambda 2457$ and between $\lambda 2449$ and $\lambda 2446$, and then transmitted to $\lambda 2144$.	Rays absorbed between $\lambda 2485$ and $\lambda 2330$ and then transmitted to $\lambda 2200$.	Rays absorbed between $\lambda 3100$ and $\lambda 2800$ and then transmitted to $\lambda 2510$.
98°	128°	168°
764 mm.	764 mm.	764 mm.
Rays absorbed between $\lambda 2462$ and $\lambda 2457$ and between $\lambda 2452$ and $\lambda 2446$, and then transmitted to $\lambda 2150$.	Rays fairly well absorbed between $\lambda 3070$ and $\lambda 2940$ and then transmitted to $\lambda 2500$.	Rays absorbed from
108°	138°	178°
764 mm.	764 mm.	764 mm.
Rays fairly well absorbed between $\lambda 2470$ and $\lambda 2350$, and then transmitted to $\lambda 2170$.	Rays well absorbed between $\lambda 3090$ and $\lambda 2900$ and then transmitted to $\lambda 2510$.	Rays well absorbed between $\lambda 3100$ and $\lambda 2800$ and then transmitted to $\lambda 2510$.

The vapour showed two weak diffuse bands at the lower temperatures and pressures. These disappear at the higher temper-

FIG. 3



tures and pressures, and two large bands take their place which are comparable with the solution bands. All the vapour bands of ethanol and benzaldehyde (*loc. cit.*) have completely disappeared,

and there is no well-marked comparison with the narrow bands of salicylaldehyde.

p-Hydroxybenzaldehyde.—The solution curve shows one large band (Fig. 3, III), which appears to take the place of the two solution bands of the ortho- and meta compounds.

The vapour of the substance showed the following phenomena:

	75°	95°	135°
	764 mm.	764 mm.	764 mm.
Rays fairly well absorbed between λ 2650 and λ 2450 and then transmitted to λ 2144.	λ 2855— λ 2400 w. and also absorbed between λ 2690 and λ 2330 and then transmitted to λ 2190.	λ 2858— λ 2838 str. and also absorbed between λ 2690 and λ 2330 and then transmitted to λ 2190.	
	85°	115°	145°
	764 mm.	764 mm.	764 mm.
Rays feebly absorbed between λ 2855 and λ 2845 and between λ 2670 and λ 2380 and then transmitted to λ 2140.	λ 2858— λ 2838 mod. str. and also between λ 2790 and λ 2320 and then transmitted to λ 2190.	λ 2855— λ 2838 mod. str. and also between λ 2790 and λ 2320 and then transmitted to λ 2190.	Rays absorbed at λ 2870

The vapour therefore showed a weak diffuse less refrangible one, and a strong wide one. The weak band does not appear in the solution. It seems as if it were merged into the large wide one, and all the vapour bands of phenol and benzaldehyde have disappeared.

The solution and vapour of anisaldehyde were also examined, as similar results were obtained to those of *p*-hydroxybenzaldehyde; all the vapour bands of anisole and of benzaldehyde had disappeared. The phenomena are, therefore, not described in detail.

o-, m., and p-Phthalaldehydes.—The comparative ease with which these substances are oxidised to the corresponding acids makes the investigation of their vapours difficult. In each case the absorption tube was filled with nitrogen, so that the oxygen present is compared with the amount of substance must have been negligible. The vapours of the substances in a 200 mm. tube showed the following phenomena:

o-Phthalaldehyde.

	Pressure in mm.	
72	760	Rays were transmitted to λ 2170.
82	760	The rays were transmitted to λ 2200; but they were almost completely absorbed between λ 2530 and λ 2200.
92	760	The rays were wholly absorbed between λ 2560 and λ 2240, and then transmitted to λ 2240.
102	760	The rays showed some signs of weakening between λ 2560 and λ 2320 and were completely absorbed between λ 2560 and λ 2320 and were then transmitted to λ 2250.
112	760	The rays were fairly well absorbed between λ 2560 and λ 2310 and then transmitted to λ 2000, from where there was complete absorption.

m-Phthalaldehyde.

80°	100°	120°
762 mm.	762 mm.	762 mm.
The rays were absorbed between $\lambda 2450$ and $\lambda 2330$ and then transmitted to $\lambda 2250$.	Rays moderately absorbed between $\lambda 2965$ and $\lambda 2945$ and then transmitted to $\lambda 2480$.	Fair absorption between $\lambda 2970$ and $\lambda 2955$ and fairly well absorbed between $\lambda 2870$ and $\lambda 2780$ and then transmitted to $\lambda 2580$.
90°	110°	130°
762 mm.	762 mm.	762 mm.
The rays were transmitted to $\lambda 2480$.	Fair absorption between $\lambda 2970$ and $\lambda 2955$ and also moderate absorption between $\lambda 2870$ and $\lambda 2780$ and then transmission to $\lambda 2500$.	Good absorption between $\lambda 2975$ and $\lambda 2940$ and between $\lambda 2885$ and $\lambda 2775$, and then transmission to $\lambda 2600$.

p-Phthalaldehyde.

86°	106°	116°
760 mm.	760 mm.	760 mm.
rays absorbed between $\lambda 2600$ and $\lambda 2350$ and then transmitted to $\lambda 2130$.	Rays fairly well absorbed between $\lambda 3050$ and $\lambda 3020$ and also between $\lambda 2960$ and $\lambda 2780$ and then transmitted to $\lambda 2640$.	Absorption between $\lambda 3080$ and $\lambda 2780$ and then weak transmission to $\lambda 2680$.
96°	126°	
760 mm.	760 mm.	
are feebly absorbed between $\lambda 3050$ and $\lambda 3020$ and strongly between $\lambda 2620$ and $\lambda 2300$ and then transmitted to $\lambda 2140$.	Complete absorption from $\lambda 3100$.	

The vapour bands of benzaldehyde, therefore, all disappear in the three compounds, and the phenomena are not unlike the solution bands.

The solution bands of the *m*- and *p*-compounds (Fig. 4, I and II) show very similar phenomena to the *m*- and *p*-chlorobenzaldehydes and the *m*- and *p*-tolualdehydes in that the *m*-compound has two bands, whereas the *p*-compound has one large more refrangible band and the less refrangible one practically disappears.

Cuminaldehyde.—The solution curve (Fig. 5, I) shows two bands which are not unlike benzaldehyde or the isomeric *o*- and *m*-tolualdehydes; but there is a greater shift towards the red end.

The vapour of the substance in a 200 mm. tube exhibited the following phenomena:

FIG. 4.

Oscillation frequencies.

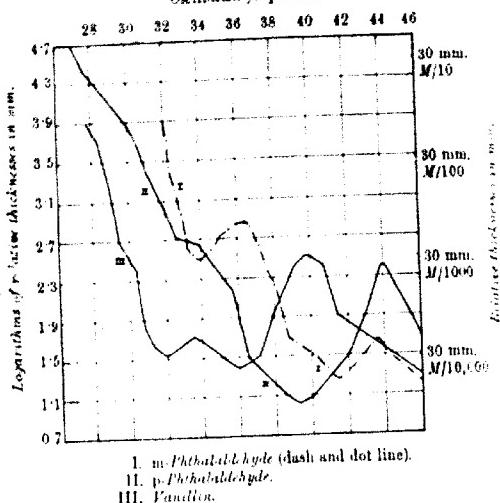
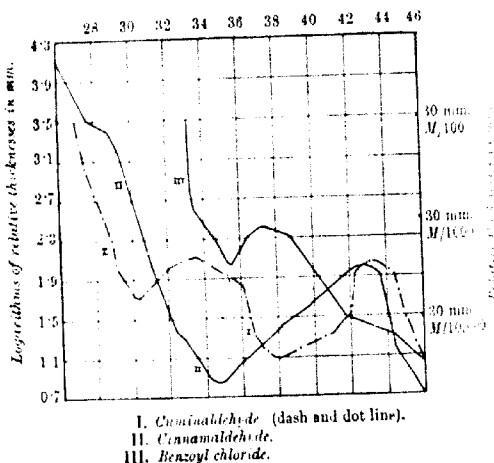


FIG. 5.
Oscillation frequencies.



Pressure in mm.		
1.	762	Rays were transmitted to λ 2140.
20	762	Rays were weak between about λ 2500 and λ 2370 and then transmitted to Cd 2144.
30	762	Rays showed signs of weakness between λ 3050 and λ 2800 and almost completely absorbed between λ 2530 and λ 2320 and then transmitted to Cd 2144.
45	762	Rays almost completely absorbed between about λ 3060 and λ 2780, and then transmitted to λ 2560, but the Cd lines 2194 and 2144 were visible.
65	762	Rays absorbed between λ 3100 and λ 2700 and then feebly transmitted to λ 2600.
70	762	Rays absorbed from λ 3150.
80	762	Rays absorbed from λ 3250.
90	762	Rays absorbed from λ 3250.

The vapour shows no trace of any of the narrow vapour bands of benzaldehyde or of the bands of any of the compounds described above. The phenomena are comparable with the solution bands.

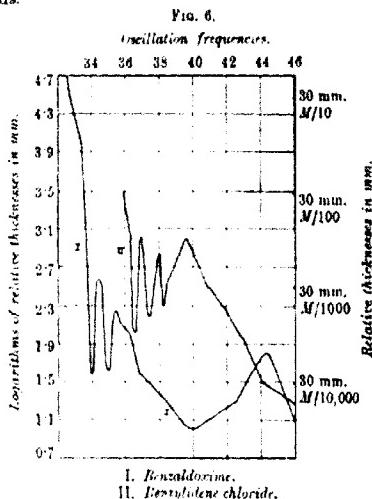
Fandlin.—The solution curve (Fig. 4, III) shows traces of two bands at $1/\lambda$ 3200 (λ 3120) and $1/\lambda$ 3600 (λ 2776), which rapidly fuse into one large band. Hartley (T., 1888, **53**, 651) found one large strong band in catechol at $1/\lambda$ 3660 (λ 2730), and the two bands of benzaldehyde are at $1/\lambda$ 3500 (λ 2855) and $1/\lambda$ 4080 (λ 2150). It appears as if there had been a fusion of these two bands into one large band.

The vapour of the substance in a 200 mm. tube showed the following phenomena:

Pressure in mm.		
90	770	The rays were weak between λ 3010 and λ 2990 and between λ 2950 and λ 2530 and then transmitted to λ 2144.
100	770	Rays fairly well absorbed between λ 3010 and λ 2990, weak between λ 2940 and λ 2850, and fairly well absorbed between λ 2670 and λ 2510 and then transmitted to λ 2144.
110	770	Rays well absorbed between λ 3010 and λ 2988, weak between λ 2950 and λ 2830, and well absorbed between λ 2700 and λ 2510 and then transmitted to λ 2180.
120	770	Rays well absorbed between λ 3010 and λ 2985, fairly well absorbed between λ 2950 and λ 2820, and completely absorbed between λ 2720 and λ 2450, and then transmitted to λ 2250.
130	770	Rays well absorbed between λ 3030 and λ 2800, and completely absorbed between λ 2730 and λ 2400 and then transmitted to λ 2270.
140	770	Rays completely absorbed between λ 3040 and λ 2350 and then transmitted to λ 2270.
150	770	Rays absorbed between λ 3050 and λ 2330 and then transmitted to λ 2290.
160	770	Rays completely absorbed from λ 3060.

There were no traces of any of the vapour bands of benzaldehyde, i.e. the six weak finer bands found in catechol (Purvis and Cleland, T., 1913, **103**, 1088) have also disappeared. The vapour phenomena are wholly comparable with the solution phenomena.

Bensaldoxime.—The solution curve (Fig. 6, I) shows two narrow bands at $1/\lambda$ 3400 (λ 2940) and at $1/\lambda$ 3500 (λ 2855). There is also some indication of a weak band between $1/\lambda$ 3570 (λ 2796) and $1/\lambda$ 3640 (λ 2745). Beyond this there is a wide strong band. Hartley and Dobbie (T., 1900, 77, 509) describe this large band but they have not described the presence of the two less refrangible narrow bands. They draw a rapid extension line between $1/\lambda$ 3650 and $1/\lambda$ 3900 (λ 2740– λ 2560), which probably indicates these bands.



The vapour of the substance in a 200 mm. tube showed the following phenomena:

Pressure in mm.		Pressure in mm.
40	769	The rays showed signs of weakening between λ 2150 and λ 2360 and were strongly transmitted to Cd 2144.
45	769	The rays were absorbed between λ 2530 and λ 2700 and then transmitted to Cd 2144.
50	769	The rays were absorbed between λ 2550– λ 2521 and then weakly transmitted to λ 2144.
60	769	The rays were transmitted to λ 2580.
75	769	The rays were transmitted to λ 2570, but they show signs of weakening between about λ 2820 and λ 2700 and between λ 2740 and λ 2720.
90	769	The rays were fairly well absorbed between λ 2820 and λ 2780, less well marked between 2740 and λ 2720 and then weakly transmitted to λ 2670, beyond which there was complete absorption.

That is to say, there were no series of fine bands comparable with those found in the vapour of benzaldehyde, and the vapour phenomena were comparable with the solution bands of benzaldoxime. It is important to notice the appearance of these narrow bands. They are not unlike several of the seven well-known benzene solution bands shifted towards the red end. It seems as if the elimination of the aldehydic oxygen in benzaldoxime had altered the oscillations producing absorption to such an extent that the benzene vibrations were partly restored.

Benzylidene Chloride.—The solution curve (Fig. 6, 11) shows three narrow bands at $1/\lambda$ 3650 (λ 2740), $1/\lambda$ 3740 (λ 2672) and $1/\lambda$ 3820 (λ 2616), which gradually widen into each other. These three bands are not unlike the three solution bands of toluene, with which they have been compared, but the large strong band into which the three toluene bands coalesce is absent, and the three bands are shifted more towards the red.

The vapour of the substance in a 200 mm. tube showed the following phenomena:

	Pressure in mm.	Pressure
75	752	The rays were a little weak between about λ 2725 and λ 2700 and between λ 2655 and λ 2640 and then transmitted to λ 2240.
45	752	The rays were moderately well absorbed between λ 2725 and λ 2700, and fairly well between λ 2655 and λ 2640, and then transmitted to λ 2260.
60	752	The rays were well absorbed between 2725 and λ 2700, fairly well between λ 2655 and λ 2640, and there were weak indications of absorption between λ 2600 and λ 2575; the rays were then transmitted to λ 2100.
15	752	The rays were absorbed from the C1 line 2748.

No series of fine bands were observed like those in the vapours of benzaldehyde or of toluene, and the weak narrow bands are comparable with the solution bands.

Benzaldehyde Sodium Hydrogen Sulphite.— $M/1000$ - and $M/10,000$ solutions of this substance were examined, and the type of absorption was exactly like that of benzaldehyde itself. That is to say, there were two bands similar in appearance to the two solution bands of benzaldehyde which have been described before (*ibid.*). As the curve is like that of benzaldehyde it has not been reproduced. The vapour of the substance could not be examined because of its easy decomposition.

Mandelonitrile.— $M/10$, $M/100$, and $M/1000$ solutions of the substance were also examined. The bands were very like the solution bands of benzaldehyde, but they were perhaps not quite so strong. The vapour was not examined because of its easy decomposition.

Benzoyl Chloride.—The solution curve (Fig. 5, III) shows that there is a weak band not unlike the solution band of benzoic acid described by Hartley and Huntington (*Phd. Trans.*, 1879, 170, 257), except that it was moved more towards the red end. The band is also not unlike the less refrangible band of benzaldehyde, but there is no appearance of the large benzaldehyde band in the more refrangible regions. The easy decomposition of benzoyl chloride made a study of its vapour impossible.

Cinnamaldehyde.—The absorption curve (Fig. 5, II) shows one large band which completely covers the area occupied by the two benzaldehyde bands.

The vapour of the substance showed the following phenomena:

Pressure	
	in mm.
15	767
30	767
45	837
60	867
75	897
90	927

The rays were transmitted to λ 2144.
The rays were almost completely absorbed between λ 275 and λ 2350 and then transmitted to λ 2144.
The rays were absorbed between λ 2850 and λ 2265 and then
feebly transmitted to λ 2194.
The rays were completely absorbed from λ 2900.
The rays were completely absorbed from λ 3000.

The vapour shows no series of fine bands characteristic of the vapour of acetaldehyde (Purvis and McCleland, T., 1913, 103, 17) or of those of benzaldehyde (*loc. cit.*). The single large band is comparable with the solution band.

General Results.

The chief results of the preceding observations are (1) that the vapours of the three chlorobenzaldehydes exhibit a considerably number of fine bands which are absent from the solutions, and fewer than those found in benzaldehyde vapour, and that the vapours of *o*- and *m*-chlorobenzaldehydes show some weak bands on the less refrangible edge of the second more refrangible band which is absent from the vapour of the *p*-compound and from the corresponding band of benzaldehyde; (2) that the vapours of the three tolualdehydes possess a few diffuse bands quite unlike those found in benzaldehyde and in the three chlorobenzaldehydes; (3) that the vapour of salicylaldehyde exhibits a number of fine bands on the less refrangible edge of the second and more refrangible band which are different from the few weak bands in *m*-hydroxybenzaldehyde and are absent in the vapour of *p*-hydroxybenzaldehyde, and that all these bands disappear in the solutions; (4) also in anisaldehyde; (4) that the vapours of the three phthaldehydes, of cinnamaldehyde, and of vanillin show no fine bands like those of benzaldehyde, and that the phenomena are like the solution phenomena; (5) that the vapours of benzaldoxime and

benzaldehyde chloride possess no finer vapour bands; the vapour phenomena and solution phenomena are similar, and indicate the presence of the residues of several benzene solution bands; (6) that solutions of benzaldehyde sodium hydrogen sulphite and of managanenitrile show absorption bands similar to those of benzaldehyde, whereas solutions of benzoyl chloride possess a weak band not unlike that of benzoic acid; (7) that the vapour of cinnamaldehyde shows none of the characteristic bands of benzaldehyde or of acetaldehyde, and that the phenomena are comparable with those of its solution; (8) that the finer bands found in the vapours of various substances at low temperatures and pressures disappear at higher temperatures and pressures, and they are replaced by bands which are comparable with the solution bands; (9) that the isomeric compounds show differences amongst themselves both as vapours and in solution, and that the para compounds exhibit the most marked differences from the ortho- and meta compounds.

In the author's previous communications the absorption spectra of numerous organic substances have been discussed from a consideration that the fundamental vibrations of any simple substance exhibiting selective absorption are influenced by such different factors as the number, the mass, the intrinsic characters and the spatial relationships of the atoms of the molecule and its side-chains, and by the physical conditions as vapours or in solution. It was shown that the fine vapour bands of such substances as benzene, aniline, and phenol become fewer or disappear altogether and fuse into one large band by the introduction of various types of side chains. The suggestion was made that the final result of the vibrations which produce selective absorption depends on the interaction of various oscillatory centres; the selective absorption of iodobenzene or of nitrobenzene, for example, is different from that in chloro- or bromo-benzene (Purvis, T., 1911, **99**, 811, 2318; Purvis and McCleland, T., 1913, **103**, 1088). The results of the observations described in this communication confirm this suggestion. It receives considerable support when benzaldoxime is considered more closely. The vapour of benzaldehyde exhibits a considerable number of fine bands. These bands are absent in the case, and both the vapour and the solution possess the residues of several benzene solution bands bordering on a strong band on its less refrangible side. It appears as if the elimination of the oxygen of the carbonyl group had enabled some portion of the vibrations of the original benzene ring to be recovered. In connexion with this line of argument it may be recalled that Hartley and Dobbie (T., 1900, **77**, 318) found that solutions of acetoxime and acetoxime had no selective absorption, whereas both

acetaldehyde and acetone possess strong absorption bands, and the paraffins themselves are quite transparent. Purvis and McCleland (T., 1912, 101, 1810) also proved that the solution band of chloroform disappears in a solution of chloral hydrate.* That different interacting groups do not act independently is also proved by the fact that benzylidene chloride possesses the remnants of three benzene (toluene) solution bands, and the absorption of benzoyl chloride is more like that of benzoic acid. Another argument is suggested by the complete absence from the vapour of cinnamaldehyde of the numerous vapour bands of benzene, benzaldehyde, and acrylic aldehyde. How far the presence of the unsaturated aliphatic group influences the final result is not yet clearly shown; but ethylene has no vapour bands in the ultra-violet regions which can be examined by ordinary photographic plates.

It has also been previously pointed out that the physical conditions of the vibrating system influence the absorption very considerably. The substances which possess a considerable number of vapour bands show no such bands in solution. Their place is taken either by a single band or by a very few which are shifted more towards the red end. The vibrations of the solvent interfere with those of the dissolved substance, and the shift towards the red may be influenced by a damping frictional resistance. The end result is also the same when the narrow vapour bands coalesce into large strong bands, as in a homologous series where the molecular weight increases (Hartley, *Phil. Trans.*, 1908, 208, 475; Purvis, T., 1910, 87, 692; Purvis and McCleland, T., 1912, 101, 1810; 1913, 103, 433), or when the number of similar side-chains is increased (Purvis, T., 1913, 103, 1638, 2283) or as in iodobenzene and nitrobenzene when the introduction of a single atom of iodine or of a single nitro group destroys all the numerous vapour bands of benzene, toluene, phenol, aniline, and aldehyde (*loc. cit.*).

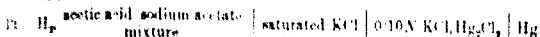
It is also to be noted that solutions of benzaldehyde sodium hydrogen sulphite and mandelonitrile show bands similar to those of benzaldehyde. These weak and unstable combinations do not essentially change the fundamental vibrations of solutions of benzaldehyde itself.

I have again to thank the Government Grant Committee of the Royal Society for their assistance in partly defraying the cost of the research.

CXXXIII.—*Hydrogen Potentials of Mixtures of Acetic Acid and Sodium Acetate.*

By GEORGE STANLEY WALPOLE.

MIXTURES of the type acetic acid-sodium acetate are largely used in certain connexions as "regulator mixtures" in the physico-chemical investigation of protein solutions. During their examination for this purpose their extremely small diffusion potential against saturated potassium chloride was noticed, and the work was, therefore, repeated with a calibrated potentiometer, and every precaution to obtain as high an order of accuracy as possible. It is hoped that these measurements will provide the necessary experimental data for an investigation of the dissociation constant of acetic acid and the dissociation of sodium acetate by the energy method. Some of them have already been used as evidence in the discussion of the vexed question of neutral salt action by McBain and Coleman (this vol., p. 1528). The cells investigated were all of the type:



although the actual measurement was made in two stages performed immediately one after the other, as will be explained later. This device in practice was more convenient, and introduced no inaccuracy into the result; rather an increased accuracy was secured thereby.

Two series of mixtures were examined, namely, (1) acetic acid-sodium acetate mixtures in which the total "acetate" was 0.20*N*, and (2) acetic acid-sodium acetate sodium chloride mixtures in which the total "acetate" was 0.20*N*, and the total sodium was 0.20*N*.

It will be seen at once that each solution of series 1 has a corresponding solution in series 2, which differs from it only in that it contains an amount of sodium chloride molecularly equivalent to the acetic acid present.

EXPERIMENTAL.

The *N*-acetic acid was standardised by titration (first trace of alk with phenolphthalein) against 0.20*N* baryta, which was itself immediately titrated against *N*-hydrochloric acid.

The *N* sodium acetate was made from material which showed no change of properties when an endeavour was made to purify it further by recrystallisation. Each sample gave in normal solution

a trace of colour with two drops of phenolphthalein solution. Samples of this sodium acetate deliberately made acid with acetic acid or alkaline with sodium hydroxide gave on repeated recrystallisation from the best "conductivity" water available, normal solutions of the same properties. Another quantity prepared from pure sodium hydroxide and acetic acid free from higher homologous acids behaved in the same manner. *E.M.F.* measurements against the 0·10V calomel electrode gave 0·7635, and 0·7785, variations which are readily accounted for by 1 part in 5,000 of acetic acid or less. They cannot have any influence on these measurements.

The solutions were first made up to have a refractive index 1·34426 at 17·5° (forty four scale divisions of Zeiss's dipping refractometer), and then adjusted by an electrometric method devised during the course of this work.

This is referred to in detail on p. 2517. On account of the poor applicability and accuracy of this method, the tedious and inaccurate sodium determinations originally employed for the standardisation were abandoned.

Apparatus.

The electromotive force measurements were made with a potentiometer by Tinsley guaranteed to have a maximum error within 1 in 10,000 at one volt. By means of a compensation arrangement embodied in the instrument measurements of less than 0·18 volt could be read to 0·1 millivolt and estimated to 0·01 millivolt. This could, in most cases, be read with precision, for the zero movement of the electrometer was banished entirely by the complete insulation of the standard cells, the accumulator and the potentiometer from each other, and the whole of the rest of the apparatus. Ten cadmium Weston cells were used, one for rough and one for more accurate measurements. The latter at the beginning and at the end of the research was checked against one with a National Physical Laboratory certificate. Its reading on both occasions was $1\cdot0183 \pm 0\cdot0001$ volt at 20°. In order to observe the movements of the mercury meniscus with precision a cover glass was cemented with Canada balsam to the glass capillary, and a combination of high magnifying power with a micrometer scale employed.

All measurements were made at 18°.

Hydrogen Electrode.

The gas electrode used for the final measurements was of the Brislee type (*Trans. Faraday Soc.*, 1905, 1, 66). A fine platinum wire burnt into the surface of Jena-glass was blackened

polyacrylic in the usual manner in a chloroplatinic acid solution containing a little lead acetate, and subsequently treated in accordance with Wilsmore's recommendations. E.M.F. readings reproducible and constant to 0·1 millivolt could be readily obtained.

In both series of solutions a preliminary exploration was made using an electrode of a simpler and more convenient type. This electrode depended on the principle discovered by Michaelis (*Biochem. Zeitsch.*, 1909, **18**, 319) that a carefully cleaned and slackened platinum wire saturated with hydrogen and placed in a hydrogen atmosphere so as just to touch the surface of a solution comes into equilibrium with it immediately. The actual form used has been recently described (*Biochem. J.*, 1914, **8**, 131).

It was found that the potentials so obtained differed seldom by more than 1 millivolt from those arrived at subsequently when the more elaborate and more accurate instrument was employed. The hydrogen purified in the usual manner and found to be free from arsenic passed through a Richardson wash flask containing some of the fluid under investigation before entering the hydrogen electrode vessel.

Calomel Electrodes.

Four 0·10*N*-calomel electrodes and four saturated electrodes were prepared at different dates prior to these determinations with the usual precautions. Of the eight calomel half electrodes one of the saturated electrodes (*A*) gave evidence of greater stability of E.M.F. than the other seven.

Method of Working.

Since the potential actually measured by the potentiometer is the sum of three potentials, every endeavour was made by suitably based independent measurements to arrange that these three potentials should be subject to independent examination and criticism. For that reason three sets of measurements were made.

*Measurements of E.M.F. between the 0·10*N* Calomel Half-electrodes and the Saturated Half-electrode A.*

The saturated half-electrode *A* was chosen as a standard throughout all these measurements because previous experience had shown its stability. This can probably be attributed to the bed of crystals of potassium chloride which had settled down in the layer of calomel and to its nine months' previous use. Its real value, referred to the four 0·10*N*-calomel electrodes prepared, was determined from time to time, and it was checked against one other of them once or twice a day. There was no evidence that

it varied in value more than 0·10 millivolt in either direction during the course of these measurements.

	May 28.	May 30.	June 2.	June 22.
A-2C	0·08834	0·08843	0·08830	0·08834
3C	0·08840	0·08860	0·08860	-
4C	0·08873	0·08875	0·08870	0·08861
4C'	0·08855	0·08856	0·08835	0·08841
Mean value	0·08851	0·08859	0·08834	0·08832

The *E.M.F.*'s of the cell made up of a theoretical 0·10*N* calomel half electrode connected to the individual saturated half electrodes (1) by means of potassium chloride solution saturated at 18°, were therefore taken as 0·0885 volt between the dates May 30th and June 22nd, 1914.

The differences in the electromotive forces given by the different 0·10*N* calomel electrodes can only be attributed to the fact that they were made up at different times from different samples of mercury, mercurous chloride, and potassium chloride, the purity of which cannot have been absolute in some cases. The figures, although discordant, demonstrate fully that the *E.M.F.* of the saturated half-electrode A was throughout these measurements constant. That the value 0·0885 is probably correct within 0·10 millivolt is suggested (1) by the measurement of the hydrogen potential of "standard acetate" (0·6016), which corresponds very closely with that of Sørensen and Koefoed, and Michaelis (0·6046), and (2) by the measurement of the same solution, to be described in a later paper, against a 0·10*N* calomel electrode of an improved and more accurate type made from specially purified materials (0·6044).

In all the above measurements of "standard acetate" Bjerrum extrapolation was applied in the usual way.

Measurements of P, that is, the E.M.F.'s of the Cells made up of the Hydrogen Half-electrodes and the Saturated Half-electrode A, with Potassium chloride solution saturated at 18° as connecting fluid.

The patterns of hydrogen electrode used have already been described. The connecting fluid was in all cases saturated potassium chloride solution maintained at 18°. On account of the extraordinarily small contact potential between these two mixtures and saturated potassium chloride it was not necessary to take precautions to renew the boundary for each observation, and in the most accurate determinations. The correction for barometric pressure was applied.

*Measurements of the Difference of Contact E.M.F. at the Boundaries ("Mixture" | 1·75*N*-Potassium Chloride) and ("Mixture" | 3·5*N*-Potassium Chloride) for each Acetic Acid-Acetate Mixture Examined.*

The side-tubes of two saturated electrodes (2*H* and 3*H*) placed *l*iacently in the same water-bath dipped into two small beakers, *s* containing 3·5*N*-potassium chloride and the other 1·75*N*-potassium chloride. These solutions were first bridged across with 75*N*-potassium chloride solution in a glass tube.

As the cell is symmetrical, the *E.M.F.* should be zero. It was usually about 0·10 millivolt in the usual case. Then, instead of using 1·75*N*-potassium chloride to link across the 1·75*N*- and the 3*N* potassium chloride solutions, the liquid under examination *is* used, and the second *E.M.F.* reading taken. The difference of these two potentials (*d*), due regard being paid to algebraic sign, is then considered to be the diffusion potential of the solution in question against saturated potassium chloride solution.

At this juncture some remarks may be made about the measurement, in two stages, of the cell indicated diagrammatically in the introduction of this paper. The circumstances which suggested this procedure, and the results in practice, tend to show that if anything a error of measurement was thereby reduced. It certainly was increased.

In the water-bath was a small vessel of saturated potassium chloride solution, and into it dipped the side tubes of the saturated electrode *A*, a 0·10*N*-calomel electrode, and the hydrogen electrode containing the fluid under examination. At first three readings *are* always taken, that is, the hydrogen electrode against each calomel electrode in turn and the calomel electrodes against each other. In the case where the fluid in the hydrogen electrode has a specific conductivity the first two measurements were fatiguing, through any minute accidental electrical leakages of the apparatus correspondingly inaccurate. On the other hand, because the low resistance of the resulting cell and the use of the multi-point shunt in the potentiometer, the measurement of the two calomel electrodes against each other is always of a high order of accuracy. It was therefore quickly discovered that, on account of the accuracy of the potentiometer exceeding that of any measurement made with it, one of the three measurements was superfluous. Direct measurement of the hydrogen electrode potential against 0·10*N*-calomel electrode was the one discarded because it was involving the higher resistance; the substitution of the indirect measurement, which in the case of good conducting fluids always

gave identical results, when the 0·10*N*-calomel electrode was corrected for its variation from the mean value of all the 0·10*N*-calomel electrodes, was preferred. Although in many cases the direct measurements against the 0·10*N*-calomel electrode were made up identical results, for the sake of uniformity and simplicity of explanation the results are expressed in the form here given.

Difficulties in Diffusion Potential Measurements.

Wohl (*Diss.*, Karlsruhe, 1905), Lewis and Rupert (*J. Am. Chem. Soc.*, 1911, **33**, 299), Cumming and Gilchrist (*Trans. Faraday Soc.*, 1913, **9**, 174), Bjerrum (*Zeitsch. Elektrochem.*, 1917, **17**, 58), and others have shown that the difference of potential between the two sides at the boundary of two dissimilar electrolytic solutions depends on the amount of mixing at the boundary at the time for which the boundary has been formed. A convention seems to be established that in order to provide data for comparative measurements these potentials should be measured for a freshly prepared boundary in relation to which no special precautions have been taken to avoid mixing.

The author has found, using the arrangement described on p. 2505, that *E.M.F.* readings varying from 3·5 to 5·5 millivolt can be observed in a few minutes if the two vessels containing 1*N*-potassium chloride and 3·5*N*-potassium chloride were linked up by means of a tube containing 0·10*N*-hydrochloric acid. Considerable experiments with this arrangement only led to concordant and consistently reproducible results with 0·10*N*-hydrochloric acid, when instead of a connecting tube, two tapes were led down, one from each potassium chloride vessel to the opposite sides of a vessel containing 0·10*N* hydrochloric acid placed at a lower level. It may be that this arrangement is the experimental realisation of the "ideal freshly prepared mixed boundary" of Cumming. As it happens, the diffusion potentials of the two series referred to in the introduction to this paper were so small that the values of *d* were the same whether glass tubes or tapes were used. On the other hand, some other solutions referred to later—an extended series 2—gave values for *d* which could not be fixed with the same order of accuracy, and hence in these cases the values of *d* (in table III) are printed in italics.

Expression of Results.

It was desired to place on record two *E.M.F.*'s with regard to each solution examined:

(1) The *E.M.F.* (*V*) of the cell:Pt | Hg₂ "solution" | saturated KCl | 0.1*N*-KCl, Hg₂Cl₂ | Hg(2) The *E.M.F.* (*E*) being the potential of the hypothetical cell:Pt | Hg₂ "solution" | 0.1*N*-KCl, Hg₂Cl₂ | Hg

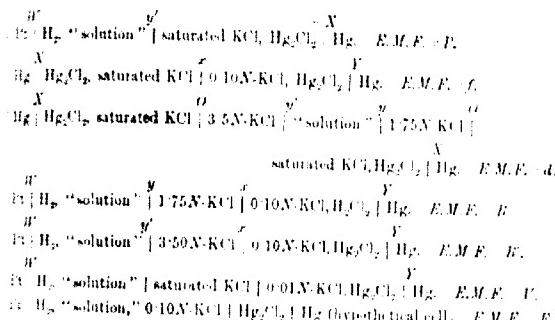
from which the contact potential at the boundary of the "solution" and 0.1*N*-potassium chloride has been eliminated by Bjerrum's extrapolation method (*Zeitsch. Elektrochem.*, 1911, **17**, 389).

A consideration of the cells indicated below will show at once that

$$V = P + 0.0885 \quad \text{---} \quad (1)$$

$$E = P + 0.0885 - d \quad \text{---} \quad (2)$$

It is assumed that no difference of potential exists between any two of the three solutions: 1.75*N*-potassium chloride, 3.5*N*-potassium chloride, and potassium chloride solution saturated at 18° C. (1*V*), and that the small unknown difference of potential between 0.1*N*-potassium chloride and any one of these solutions is a constant value *x*, a quantity which it will be seen cancels out in the equations above:



The *E.M.F.* (*E*) of the hypothetical cell No. 7 above, according to Bjerrum's extrapolation method, is $2B' - B$:

$$E = 2B' - B$$

$$= W - Y + 2y' + x - y.$$

Also from the equations above:

$$\begin{aligned} -(P + f - d) &= W - Y + 2y' + x - y; \\ \text{before } E &= P + f - d, \\ &= P + 0.0885 - d. \end{aligned}$$

That is to say, equations (1) and (2) hold, and the method of applying Bjerrum's extrapolation method used in these measurements can differ in no way, in the actual result reached, from that Sorenson and other workers.

Series I.

Acetic Acid-Sodium Acetate Mixtures: Total "Acetate" is 0·20 Normal.

In order to prepare each solution n c.c. of *N*-acetic acid ($20-n$) c.c. of *N*-sodium acetate were mixed and diluted to 100. Where n or ($20-n$) was small, suitable precautions were taken to measure the volumes accurately. A comparatively large volume of the normal solution was diluted ten- or one hundred-fold, and or $\frac{1}{10}$ hundred times this volume taken. The results of measurements of V and d for these solutions are given in tab. Figures in brackets are obtained by extrapolation on accurate squared paper. Where more than one measurement is given, results are from different preparations of *N*-sodium acetate, *N*-acetic acid on different dates. The particular mixture 10 c.c. *N*-acetic acid + 10 c.c. of *N*-sodium acetate diluted to 100 c.c. "standard acetate"—was measured whenever an electrode was blackened or new standard solutions were prepared. The consistent result ($P : 0\cdot0885$)—0·6047, which when corrected for dissociation potential becomes 0·6046, is in good accord with the correct result 0·6045, which is the result for the same mixture as determined by Sørensen and Koefod and by Michaelis. The frequent repetition of this determination was adopted as an additional safeguard against the errors which are apt to enter into determinations of this kind.

According to the theory of mass action applied to the partially dissociated acetic acid the relationship

$$[\text{H}^+] = \frac{k_a C}{a^2} \quad \dots \dots \dots \dots \dots \dots$$

should hold; and it is interesting to examine over what range ratios of acetic acid and sodium acetate the hydrogen potential against the 0·10*N*-calomel electrode may be calculated.

To do this the right hand expression of (3) is substituted in the well-known energy equation:

$$E.M.F. = \epsilon_0 + \frac{RT'}{F} \log_{10} \frac{1}{[\text{H}^+]} \quad \dots \dots \dots \dots \dots \dots$$

$$= 0\cdot3377 - 0\cdot0577 \log_{10} \left(\frac{k_a C}{a^2} \right) \quad \dots \dots \dots \dots \dots \dots$$

For calculating a Kohlrausch's conductivity measurements can be used, and $18\cdot83 \cdot 10^{-6}$ * may be taken as the dissociation constant of acetic acid at 18°. Sørensen's value for ϵ_0 at 18° has been

* This is a purely arbitrary value chosen so that the calculated $E.M.F.$ of "standard acetate" will agree with the observed value.

MIXTURES OF ACETIC ACID AND SODIUM ACETATE 2509

$C.$	Concentration of acetic acid.	V_{large} ($V + 0.0885$)	V_{small} ($V + 0.0885$)	d .	$\frac{V}{V+d}$ $0.0885 - d$,	$\frac{V}{V+d}$ 0.0885	$\frac{V}{V+d}$ (Kohlrausch)	Difference between calculated and experi- mentally determined values of E .	P^{a}
0.00028N	0.1992N	0.7785	0.00015	—	—	57.1	57.1	—	—
0.0002	—	—	—	—	—	57.1	57.1	—	—
0.0005	0.1995	—	—	—	—	57.1	57.1	—	—
0.001	0.199	—	—	—	—	57.1	57.1	—	—
0.0025	0.1975	—	—	—	—	57.1	57.1	—	—
0.003	0.195	—	—	—	—	57.1	57.1	—	—
0.0075	0.1925	—	—	—	—	57.1	57.1	—	—
0.01	0.19	—	—	—	—	57.1	57.1	—	—
0.02	0.18	—	—	—	—	57.1	57.1	—	—
0.03	0.17	—	—	—	—	57.1	57.1	—	—
0.04	0.16	0.6475	0.6479	(0.00013)	0.6478	(57.9)	0.6482	0.0011	2.67.10 ⁻⁴
0.05	0.15	—	—	—	—	58.1	0.6470	0.0008	4.23.10 ⁻⁴
0.06	0.14	—	—	—	—	58.6	0.6383	0.0010	5.93.10 ⁻⁴
0.08	0.12	0.6136	0.6149	(0.0001)	0.6148	(59.0)	0.6313	0.0003	8.07.10 ⁻⁴
0.10	0.10	0.6137	0.6147	(0.0001)	0.6147	(59.4)	0.6251	0.0005	1.02.10 ⁻³
0.10	0.10	0.6047	0.6047	(0.0001)	0.6046	(61.1)	0.6046	0.0004	2.37.10 ⁻⁴
0.10	0.10	0.6047	0.6047	(0.0001)	0.6046	(61.1)	0.6046	0.0004	4.626

3

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TABLE I (*continued*).

Concentration of acetic acid	$\frac{V_{\text{cell}}}{V_{\text{cal}}}$	Concentration of sodium acetate	$\frac{V_{\text{cell}}}{V_{\text{cal}}} \cdot 0.0855$	$\frac{E_{\text{cell}}}{E_{\text{cal}}} \cdot 0.0855 - 1.0$				Difference between calculated and experimentally determined values of E_{cell}
				$\frac{E_{\text{cell}}}{E_{\text{cal}}} \cdot 0.0855 - 1.0$	$\frac{\mu_{\text{H}}}{\mu_{\text{H}}^{\text{cal}}} \cdot 0.0855 - 1.0$	$\frac{E_{\text{cell}}}{E_{\text{cal}}} \cdot (\text{Kohlrausch})$ (calculated by equation 5)	$\frac{E_{\text{cell}}}{E_{\text{cal}}} \cdot (\text{Kohlrausch})$ (calculated by equation 5)	
0.12	0.08	{ 0.530 0.537 }	{ 0.537 0.547 }	0.00005	—	0.5847	0.5842	-0.0001
0.14	0.06	{ 0.5832 0.5841 }	{ 0.5841 0.5841 }	0.00005	—	0.5841	0.5841	—
0.16	0.04	{ 0.5707 0.5712 }	{ 0.5712 0.5712 }	0.00005	—	0.5712	0.5714	-0.0002
0.18	0.02	{ 0.5521 0.5525 }	{ 0.5525 0.5525 }	0.00005	—	0.5525	0.5522	-0.0003
0.185	0.015	{ 0.5450 0.5450 }	{ 0.5450 0.5450 }	0.00005	—	0.5450	0.5447	-0.0003
0.190	0.010	{ 0.5348 0.5348 }	{ 0.5348 0.5348 }	0.00005	—	0.5348	0.5343	-0.0005
0.192	0.008	{ 0.5290 0.5290 }	{ 0.5290 0.5290 }	0.00005	—	0.5290	0.5288	-0.0002
0.194	0.006	{ 0.5225 0.5225 }	{ 0.5225 0.5225 }	0.00005	—	0.5225	0.5216	-0.0009
0.195	0.005	{ 0.5193 0.5193 }	{ 0.5193 0.5193 }	0.00005	—	0.5193	0.5179	-0.0013
0.196	0.004	{ 0.5155 0.5155 }	{ 0.5155 0.5155 }	0.00005	—	0.5155	0.5115	-0.0040
0.197	0.003	{ 0.5105 0.5105 }	{ 0.5105 0.5105 }	0.00005	—	0.5105	0.5044	-0.0061
0.198	0.002	{ 0.5057 0.5057 }	{ 0.5057 0.5057 }	0.00005	—	0.5057	0.4943	-0.0114
0.199	0.001	{ 0.4995 0.4995 }	{ 0.4995 0.4995 }	0.00005	—	0.4995	0.4771	-0.0224
0.200	0.000	{ 0.4934 0.4934 }	{ 0.4934 0.4934 }	0.00005	—	0.4934	0.4931	-0.0006

adopted. The results calculated according to this equation are given in column 8 of table I. The difference between the observed values and the calculated values is given in the next column. It must not be considered that these are errors in potential determinations. Their theoretical significance is connected with those problems in connexion with which these measurements were undertaken. As a matter of interest it may be here recorded that in series I the values of E for those solutions of composition between

C	C'	Ratio C/C'	$[H^+]$	P_H^+	E
0.0075 <i>N</i>	0.1923	0.039	$9.46 \cdot 10^{-7}$	6.024	0.6844
0.1940 <i>N</i>	0.0060	32.3	$8.28 \cdot 10^{-4}$	3.202	0.5216

may be calculated with an error not exceeding one millivolt from equation (4) above.

In columns 10 and 11 are calculated, from the observed $E.M.F.$'s corrected for diffusion potential, the hydron concentrations and the hydrogen-ion coefficient (P_H^+) on the basis $\epsilon_A = 0.3377$ and $K = 0.0577$.

With regard to the value of E for pure sodium acetate it has been calculated on the basis of 0.008 per cent. of hydrolysis (compare Walker, *Zeitsch. physikal. Chem.*, 1900, **32**, 138). The large divergence between the experimentally determined values of E for the two samples of pure sodium acetate examined has been already discussed (p. 2502). The discrepancy between these determinations and the calculated value of E may be attributed to similar causes.

At the other end of the series the divergence between the calculated and observed values when the ratio C/C' exceeds 32.3 may once be attributed to the incorrectness of one of the original assumptions in this case. The total $[Ac']$ concentration in such solutions is no longer represented with sufficient approximation by C .

The magnitude of the differences in column 9 of table I suggests a search for an expression which will represent still more accurately the relationship between the hydron concentration $[H^+]$ and the composition of these acetic acid-sodium acetate mixtures. We may write first of all

$$[H^+] = \frac{k_a [HAc]}{[Ac']}$$

Instead of $[HAc]$, the concentration of the undissociated acetic acid, may be substituted $(C - [H^+])$; and, as an attempt at expressing $[Ac']$ in terms of a , C , and $[H^+]$, the relationship

$$[Ac'] = a'C' + [H^+]$$

where a' is the value a applied, not to C' (the concentration of sodium acetate) as before, but, in accordance with Ostwald's isopiestic principle to the acetic-ion concentration $[Ac']$.

The completed formula is therefore

The solution of this equation for $[H^+]$ does not give a simple expression, and, as $[H^+]$ is a small quantity, its occurrence in the numerator and denominator of this expression is more conveniently left undisturbed, and the calculation performed by the method of trial and error.

In this way the value of $[H']$ is found, which, when substituted into the expression $\frac{\mu_0}{C} \left(\frac{k_0(C - [H'])}{[H']} - [H'] \right)$ gives a result μ_{NaAc} , which is equal to the value of μ corresponding with a sodium acetate concentration of $\left(\frac{k_0(C - [H'])}{[H']} \right)$ in Kohlrausch's tables.

From the values of $[H^+]$ so calculated the values of E were obtained by means of equation (4).

Examination of equations (3) and (6) shows that when $C = 0$ the former becomes indeterminate, but the latter simplifies to the equation:

$$\{H^*\} = \sqrt{k_a(C - H^*)}$$

TABLE II.

C = concentration of acetic acid.	$E = \text{observed } E.M.F.$ against decimal normal electrodes corrected for diffusion potential.	E calculated by equations (6) and (4) above.	Difference between calculated & observed values.
0.0025	0.7138	0.7132	+ 0.0006
0.005	0.6951	0.6955	+ 0.0006
0.0075	0.6853	0.6851	+ 0.0002
0.01	0.6778	0.6776	+ 0.0002
0.02	0.6593	0.6590	+ 0.0003
0.03	0.6478	0.6475	+ 0.0003
0.04	0.6393	0.6389	+ 0.0004
0.05	0.6318	0.6318	0.0000
0.06	0.6256	0.6256	0.0000
0.08	0.6148	0.6148	0.0000
0.10	0.6046	0.6050	- 0.0004
0.12	0.5947	0.5953	- 0.0006
0.14	0.5841	0.5848	- 0.0003
0.16	0.5712	0.5718	- 0.0006
0.18	0.5525	0.5526	- 0.0001
0.185	0.5450	0.5455	- 0.0005
0.190	0.5348	0.5354	- 0.0006
0.192	0.5290	0.5303	- 0.0013
0.194	0.5225	0.5240	- 0.0015
0.195	0.5193	0.5204	- 0.0011
0.196	0.5155	0.5163	- 0.0008
0.197	0.5105	0.5117	- 0.0012
0.198	0.5057	0.5062	- 0.0005
0.199	0.4995	0.5005	- 0.0010
0.200	0.4931	0.4943	- 0.0012

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which is the expression for the hydron concentration of an acetic acid solution of concentration C.

The results of using equations (4) and (6) for calculating the hydrogen potentials of acetic acid-sodium acetate mixtures against the 0.10V-calomel electrode are given in column 3 of table II. C' is, of course, (0.20-C), and the values of k_s (18.83×10^{-6}), Kohlrausch's values for α , and the constants are taken as before.

An expression based on the law of mass action has, therefore, been found, by which the E.M.F.'s of the "0.20V-total acetate" series of acetic acid-sodium acetate mixtures may be calculated accurately. The observed values for the series from $C/C' = \infty$ to $C/C' = 0.039$ differed from the calculated values by a maximum of 1.5 millivolt in a single instance.

It is not possible at present to go yet further and investigate the significance of these differences and their gradual change of sign as we pass from one end of the series to the other, for the uncertainty of the dissociation of sodium acetate at different dilutions is greater than the calculated discrepancies.

Series II.

Acetic Acid-Sodium Acetate Sodium Chloride Mixtures: Total Acetate 0.20 Normal, Total Sodium 0.20 Normal.

Each solution was prepared by adding m c.c. of N-hydrochloric acid to 20 c.c. of N-sodium acetate, and diluting the mixture to 50 c.c.

The results are given in table III, which, since it is arranged in a similar fashion to table I, needs little further explanation. In column 1 are given the values of m , and in columns 2, 3, 4, 5 the compositions of the resulting mixtures in terms of acetic acid, sodium acetate, sodium chloride, and hydrochloric acid.

It will be shown later that some of these mixtures would give accurate results if prepared in this way. In the region of "20 c.c. hydrochloric acid + 20 c.c. N-sodium acetate" they were prepared by mixing N-acetic acid and N-sodium chloride with either hydrochloric acid or N-sodium acetate in the right proportion. The greatly increased accuracy of this method of procedure will be clear from the explanation on p. 2517.

As a check on the purity of the reagents and the accuracy of their standardisation, not only this part of the series, but the whole of the determinations were repeated, from $m=0.4$ to $m=22$, three four times with the solutions prepared in different manners as the various possible constituents, sodium hydroxide, acetic acid, sodium acetate, hydrochloric acid, and sodium chloride. The

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TABLE III.

μ	Concentration of sodium acetate	Concentration of sodium chloride	Concentration of hydrochloric acid	$p + 0.0855 \cdot \gamma$	$p + 0.0855 \cdot \gamma$	$[H]$
0.40	0.196	0.004	0.7017	0.00016	0.7015	6.31
1.05	0.0104	0.0105	0.6763	(0.00012)	0.6762	6.87
2.00	0.0195	0.0195	0.6375	(0.00013)	0.6375	7.30
3.00	0.04	0.04	0.6235	(0.00013)	0.6235	7.85
4.00	0.14	0.06	0.6125	(0.00007)	0.6126	8.40
6.00	0.06	0.08	0.6017	(0.00017)	0.6016	8.76
8.00	0.08	0.12	0.6017	(0.00016)	0.6016	9.10
10.00	0.10	0.10	0.5903	(0.00025)	0.5903	9.39
12.00	0.12	0.12	0.5730	(0.00029)	0.5730	9.79
14.00	0.14	0.14	0.5631	(0.00031)	0.5631	10.19
16.00	0.16	0.16	0.5560	(0.00031)	0.5560	10.54
17.00	0.17	0.17	0.5517	(0.00038)	0.5517	10.61
18.00	0.18	0.18	0.5385	(0.00037)	0.5385	10.49
18.50	0.185	0.185	0.5327	(0.00031)	0.5327	10.33
19.00	0.189	0.189	0.5270	(0.00031)	0.5274	10.20
19.40	0.190	0.190	0.5153	(0.00031)	0.5150	10.09
19.50	0.194	0.194	0.5125	(0.00035)	0.5129	10.04
19.55	0.195	0.195	0.5115	(0.00035)	0.5119	10.03
19.59	0.195	0.195	0.4945	(0.00035)	0.4949	9.72
19.60	0.195	0.195	0.4898	(0.00035)	0.4903	9.64
19.69	0.199	0.199	0.4712	(0.00025)	0.4715	9.32
20.00	0.200	0.200	0.4639	(0.00008)	0.4630	9.03
20.39	0.2000	0.2000	0.4549	(0.00008)	0.4526	8.77
20.89	0.2000	0.2000	0.4455	(0.00002)	0.4426	8.50
21.00	0.2000	0.2000	0.4453	(0.00002)	0.4372	8.43
21.40	0.2000	0.2000	0.4375	(0.00002)	0.4328	8.24
21.50	0.2000	0.2000	0.4365	(0.00002)	0.4303	8.10
22.00	0.2000	0.2000	0.4200	(0.00002)	0.4194	7.71
22.00	0.2000	0.2000	0.4203	(0.00002)	0.4197	7.42
22.00	0.2000	0.2000	0.4105	(0.00015)	0.4080	7.84
22.00	0.2000	0.2000	0.4090	(0.00015)	0.4067	8.09
22.00	0.2000	0.2000	0.4025	(0.00017)	0.4017	8.97
22.00	0.2000	0.2000	0.3935	(0.00017)	0.3916	9.35
22.00	0.2000	0.2000	0.3840	(0.00017)	0.3821	9.61
22.00	0.2000	0.2000	0.3745	(0.00017)	0.3726	9.81

results were consistent to within a millivolt or two. With increasing experience the discrepancies between different *E.M.F.* determinations with the same solution prepared from different materials became less. This constant repetition was made possible by the use of the smaller and more rapidly working type of electrode. The main points were afterwards checked by the larger and more accurate electrode. The *E.M.F.* measurements at these points are in heavier type. They have been utilised by McBain (*loc. cit.*) in support of his views on neutral salt action. He points out that of the 2.9 millivolt difference of hydrogen potential resulting from the addition of 0.20*N*-sodium chloride to 0.20*N*-acetic acid either 1.1 or 1.6 millivolts is accounted for on the principle of hydrochloric acid. This would leave a small but definite increase in acidity of 1.8 or 1.3 millivolts to be ascribed to an enhancement of the dissociation constant of acetic acid by the sodium chloride.

At other points the series, although carefully examined, may have one or two errors up to ± 1.0 millivolt, and cannot claim the higher order of accuracy pertaining to series I, which was investigated later. Those results placed in italics were obtained at the commencement of this investigation, and, unfortunately, through lack of time, it was impossible to check them afterwards. They may possibly be incorrect by several millivolts. The diffusion potentials for these determinations are also open to suspicion. I have included them solely because it is of interest to trace the course of the curve complete from $m = 0$ to $m = 40$.

Diagrammatic Representation of Results in Series I and II (Fig. 1).

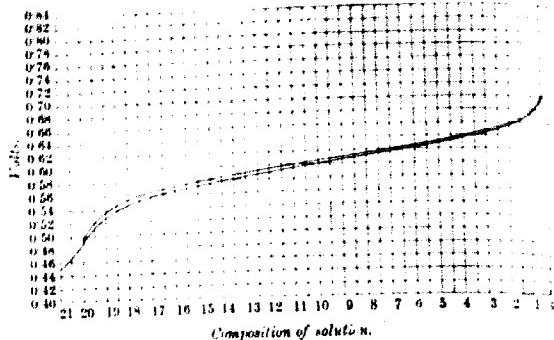
In Fig. 1 are shown two curves, of which the upper one expresses the relationship between the figures in columns 1 and 6 in table I. The curve connecting the calculated values in column 3 of table II and the values of *C* in column 1 of the same table lies so closely on this curve that in the reproduction it cannot be seen. The lower one expresses the relationship between the c.c.'s of *N*-hydrochloric acid (*m*) added to 20 c.c. of *N*-sodium acetate, the mixture subsequently being diluted to 100 c.c., and the fully corrected potential against the 0.10*N*-calomel electrode of a hydrogen electrode in equilibrium with the diluted solution (see table III).

The Effect of Twenty-fold Dilution on the Hydrogen Potential of Solutions in Series I and II.

Except in the cases of pure sodium acetate and mixtures containing only traces of acetic acid, the hydrogen potential of all the

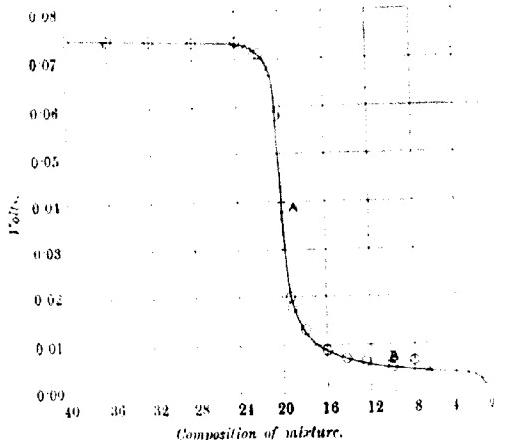
solutions dealt with in this paper increases with dilution. In Fig. 2 a curve is plotted demonstrating the relationship between

FIG. 1.



the change of E.M.F. on dilution and the composition of the mixture diluted. Within a fraction of a millivolt the right-hand

FIG. 2.



half of this curve serves for both series. As ordinates are plotted the change of E.M.F. on twenty-fold dilution, and, as abscissæ numbers representing, as in Fig. 1, the composition of the solutio-

in question. Points *A* and *B*, representing the change of *E.M.F.*, corrected for diffusion potential, on twenty-fold dilution, of 0·20*N*-acetic acid and "standard acetate" respectively, have been determined with the highest possible accuracy, using special electrodes and a silica electrode vessel. These form part of a series of determinations to be published in a later paper.

It will be seen that the rough statement that the hydrogen potential of acetic acid-acetate mixtures is independent of dilution holds rigidly for only one particular acetic acid acetate mixture, and is, with the exception of solutions approximating in composition to pure sodium acetate, more nearly correct for solutions that are more alkaline than those which are more acid than "standard acetate."

The Electrometric Standardisation of Sodium Acetate.

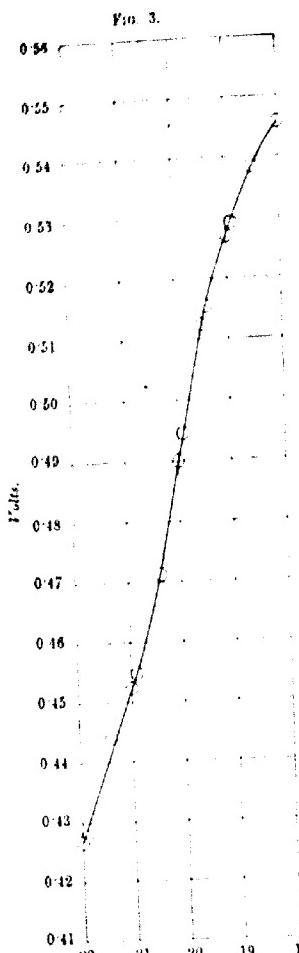
If 20 c.c. of *N*-hydrochloric acid and 20 c.c. of *N*-sodium acetate are mixed, an error of 1 in 1000 in the relative strengths of the hydrochloric acid and sodium acetate solutions, or in the measurement of either, would produce an error of 0·94 millivolt in the potential reading of a hydrogen electrode in equilibrium with the solution. Now this mixture, if the measurement of the liquids is theoretically exact, is a solution which is 0·20*N* with respect to both sodium chloride and acetic acid. In spite of its sensitiveness to strong acids, and the salts of strong bases and weak acids, it can be reproduced readily with great exactness from pure *N*-sodium chloride and *N*-acetic acid, and, moreover, since

$$[\text{H}^+] = \sqrt{k_a[\text{HAc}]} = \sqrt{k_a(\text{C} - [\text{H}^+])},$$

a slight error in the concentration of the acetic acid will have a still smaller effect on the hydron concentration of the solution.

These facts have been made the basis of the method employed to prepare *N*-sodium acetate solution. I have adopted the definition: "Normal sodium acetate solution is a solution of pure sodium acetate of such concentration that when 20 c.c. are taken, mixed with 20 c.c. of *N*-hydrochloric acid, and diluted to 100 c.c., the potential of a hydrogen electrode in equilibrium with it is the same as that of a hydrogen electrode in equilibrium with a solution 0·20 normal with respect to both acetic acid and sodium chloride."

To facilitate the preparation of normal sodium acetate in accordance with this definition a small part of the lower curve of Fig. 1 is reproduced in Fig. 3 on a different scale. The *E.M.F.*. values have been taken, however, from column 6, and not column 8, because therefore the direct results obtained against the decinormal electrode when the connecting fluid is saturated potassium chloride dilution. The rapid change of *E.M.F.* with the composition of the



may be made readily, with certain accuracy to a fraction of a millivolt, this method of standardising sodium acetate will

solution in the neighbourhood of "20 c.c. of *N*-hydrochloric acid + 20 c.c. of *N*-sodium acetate diluted to 100 c.c." is at once apparent. The curve is here a straight line, and the correction for 1 per cent. error in adjustment of the two solutions is 9.4 millivolts.

To illustrate the method employed to determine the exact concentration of an approximately normal sodium acetate solution an actual example may be given.

Twenty c.c. of *N*-hydrochloric acid were mixed with 20 c.c. of the sodium acetate solution to be standardised and the mixture diluted to 100 c.c. This diluted solution was in equilibrium with a hydrogen electrode, 0.4800 v.d. against a 0.10*N*-calomel electrode.

Referring to the curve it is seen that the ratio

$$\frac{(\text{concentration of hydrochloric acid})}{(\text{concentration of sodium acetate})}$$

is 20.20/20.00. Hence the concentration of the sodium acetate solution is 0.9954 and in use, whenever a certain volume, say, x c.c., of 1*N* sodium acetate are required there must be measured $\frac{x}{20.20}$ c.c. of this solution, i.e. $\frac{x}{20.20}$ c.c. of the same solution 10 times diluted.

As consecutive different measurements of this E_{H^+}

may be trusted to the extreme limits of precision of volumetric measurement as ordinarily applied.

Throughout all the determinations in this work the normal standard acetate solution used was adjusted to an accuracy of 1 in 1000 in accordance with the electrometric definition given above.

The Preparation of "Standard Acetate" Solution.

There are now available two methods of preparing "standard acetate":

(1) From *N*-sodium hydroxide solution free from carbon dioxide and *N*-acetic acid adjusted by a suitable titration (using phenolphthalein), so as to be exactly equivalent to it.

(2) From *N*-sodium acetate and *N*-acetic acid adjusted by a titration of a baryta solution (see p. 2501), the strength of which is known exactly in terms of the *N*-hydrochloric acid solution used to standardise electrometrically the normal solution of sodium acetate.

As the accuracy of the hydron concentration of the "standard acetate" solution depends to a greater extent on the exact equivalence of the amounts of sodium acetate and acetic acid present than on their absolute amount, the relative accuracies with which *N*-hydrochloric acid and *N*-sodium hydroxide can be prepared is a question which does not enter into these considerations. There does not appear to be any evidence that either of the methods (1) or (2) above is the more accurate, although for the preparation of *N*-sodium acetate solution itself the second method is to be preferred.

In table I it is seen that the mean of the hydrogen potential measurements for $C=0\cdot08$ and $C=0\cdot12$ is within a tenth of a millivolt of the same value for $C=0\cdot10$, that is, "standard acetate." In other words, the upper curve of Fig. 1, which represents these measurements, is, between these points, a straight line. Also, it will be shown in a later paper that the change of this potential resulting from a change of concentration of "standard acetate" variation in the ratio y is exactly $\log y \cdot 262\cdot1$ volts. Hence, if in an attempt to prepare "standard acetate" one solution be measured with theoretical accuracy and be of exact normal strength, and the other be x per cent. incorrect either in its standardisation or in its measurement, the difference of hydrogen potential in volts between the resulting sodium acetate-acetic acid mixture and that of the "standard acetate" will be:

$$\frac{x}{20}(0\cdot6148 - 0\cdot6046) \pm \frac{1}{262\cdot1} \log \left(\frac{100+x/2}{100} \right).$$

The choice of algebraic sign, + or -, will depend on whether

the incorrectly measured solution is the sodium acetate or the acetic acid, and whether its strength is α per cent. greater than or α per cent. less than normal. In practice, however, the right-hand part of this expression may be ignored entirely, for even when $\alpha = 6$ its value only reaches 0.05 millivolt, and the statement made with all practical accuracy that an error of 1 per cent. made in the standardisation of either solution or its measurement will lead to an error of 0.51 millivolt in the hydrogen potential of the resultant "standard acetate," and the relationship between the percentage error in standardisation or measuring one of the solutions and the resultant potential error, is one of simple proportion.

In view of these remarks it is the more easy to accept the convincing experience that with either of the two methods described it is possible to reproduce "standard acetate" with great accuracy. The most searching hydrogen potential measurements can barely detect with certainty differences between different preparations of this solution. On this account and because of a very small contact potential (which connotes a negligible "time change") against potassium chloride solutions, Michaelis's recommendation of it as the most suitable solution for checking the working of hydrogen electrodes can be confirmed. It should, of course, be remembered that the *N*-acetic acid solution and the acetic acid from which the *N*-sodium acetate solution is made must be known purity.

Summary.

The contact *E.M.F.* between acetic acid-sodium acetate mixtures and a potassium chloride solution is of the order of 0.10 millivolt. Hydrogen *E.M.F.* measurements, corrected for this small potential difference by Bjerrum's extrapolation method, have been made of a series of these mixtures against the 0.10*N*-calomel electrode. With these have been compared the calculated results obtained by the well known energy relationship and Fels's original equation. By the introduction of three rational corrections to this equation, two of them based on the principle of isohydrysm, calculated results have been obtained agreeing with those observed to within 1.5 millivolt or less over the whole range from pure acetic acid to a mixture containing thirty-two times as much sodium acetate as acetic acid. The original equation is less accurate than the new equation for solutions containing much sodium acetate, and is grossly inaccurate for mixtures approximating to pure acetic acid in composition. For pure acetic acid Fels's equation is indeterminate, whereas the new equation simplifies to the correct expression for the hydrogen concentration of acetic acid in terms of its dissociation constant and its concentration.

A second series identical with the first, excepting only that sodium chloride was present in concentration equal to the acetic acid, has also been examined.

Determinations have also been made of the change of hydrogen potential of these series of solutions on twenty-fold dilution. The statement that the hydrogen potential of acetic acid-acetate mixture is independent of dilution holds rigidly for only one particular acetic acid-acetate mixture, and is, with the exception of solutions approximating in composition to pure sodium acetate, more nearly correct for solutions that are more alkaline than those which are more acid than "standard acetate."

An electrometric method of standardising sodium acetate capable of development to a high order of accuracy has been devised and described. Using this method, the hydrogen electrode *E.M.F.* of the "standard acetate" solution of Michaelis can certainly be reproduced to within ± 0.10 millivolt, and probably with even a higher order of accuracy.

WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HURST HILL, LONDON, S.E.

XXXIV.—*The Effect of Dilution on the Hydrogen Potentials of Acetic Acid and "Standard Acetate" Solutions.*

By GEORGE STANLEY WALPOLE.

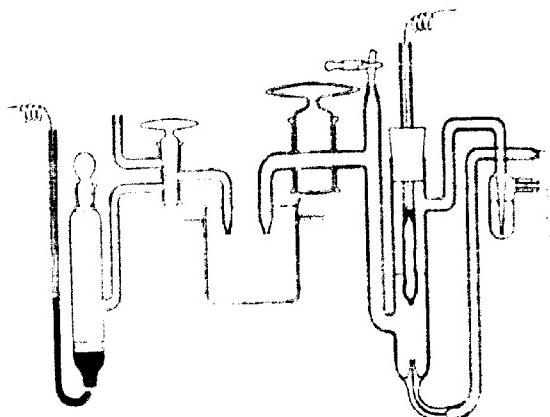
THE measurements described in this paper form a continuation of the work already detailed in the preceding one. Several alterations were made in the technique and apparatus employed with a view to increase if possible the accuracy of the results.

The potentiometer used was made by Tinsley, and had two dials. The first read 0.1 volt for each coil, and the second, acting as a counter on the Thomson-Varley slide principle, read 0.01 volt for each coil. A light travelling contact of platinum, actuated from outside the instrument by a silk cord, pressed evenly on two similarly placed wires. One of these was the slide wire of the potentiometer. The other was a similar wire, to which the electrode was connected. All junction and thermo-electric effects were therefore neutralised. Three cm. of the slide wire corresponded with a millivolt in the potentiometer reading without the use of a multiplying shunt. The instrument was guaranteed correct to 1 in

100,000 at the reading 1 volt, and certainly contained no inaccuracy which could affect these measurements.

The perfect insulation of the instrument in addition to the precaution of isolating all parts of the apparatus on par^a, banished the "zero movement" of the electrometer so completely that even with the powerful optical arrangement employed it could not be detected. On one or two damp days, however, a movement of the meniscus could be observed on opening the key short-circuiting the electrometer, and the work was, for that reason, temporarily suspended.

The electrode vessel employed was entirely of silica, and was made specially for these determinations. It was of the conventional



pattern, except that the side-tube connecting its contents with the saturated solution of potassium chloride was of wide bore (7.5 mm.) and carried a full bore silica tap. This was essential in view of the low conductivity of some of the solutions to be examined. The electrodes themselves were made by blackening a film of platinum burnt on to the surface of the hardest Jena glass. In this way it was arranged that when once the solution was placed inside the electrode vessel it came into contact with nothing but platinum or silica.

In order to make an observation, the carefully prepared electrode which had been standing in the experimental fluid, was transferred to the electrode vessel, which was filled to such an extent that the blackened platinum surface was completely covered. By this

was passed through the fluid for twenty-five minutes, and then so much of the fluid forced out through the side-tube that only one third of the electrode remained immersed. After another five minutes, during which hydrogen was passed slowly, the stream of gas was stopped and a reading taken. It was demanded of every electrode employed that it should then give at once a potential constant to 0.05 millivolt for at least half an hour, and that another electrode should give within less than 0.10 millivolt the same reading when they were tested in the same well-conducting fluid of known stability of reaction, for example, "standard acetate." Electrodes of the type used satisfying these conditions could be prepared with comparative ease.

The Silica Syndicate of London, who made the silica vessel, kindly prepared some silica electrodes with platinum burnt on the surface, but these were not so successful. Possibly this was because it was impossible to lead the platinum film through the silica as had been done with the glass electrodes. They were therefore caused to make contact between the inside and the outside of the electrode by means of a fine metallic wire leading through the silica, thus sacrificing what would appear to be the cause of the superiority of these electrodes, namely, the uniform thinness of the layer of metallic platinum on which the platinum black is deposited.

All hydrogen potential readings were corrected for barometric variation. If the barometer reading was x mm., then $(760 - x) 0.017$ millivolt was added to the potentiometer reading obtained, due attention being paid to the algebraic sign. This correction during these experiments never exceeded 0.15 millivolt, and was usually much less.

The method of working was to determine all potentials against a special 0.10*N*-calomel electrode *G*. In order to avoid any risk of variation in the potential of this electrode in use, the Wilsmore three-way tap device was employed, and the vessel clamped so firmly that the daily rinsing of the side-tube could be performed without mechanical shock or vibration. The copper wire leading into the mercury in the second side-tube was not disturbed at any time. The calomel and the 0.10*N*-potassium chloride solution in the electrode vessel were prepared with the usual precautions. The side-tubes of both this electrode and the hydrogen electrode dipped into a vessel containing 4.10*N*-potassium chloride. The water-bath containing this vessel and the calomel electrode was kept at $18^{\circ} \pm 0.1^{\circ}$ for several hours before any readings were taken and during the observations, so that the calomel electrode might be given every opportunity of giving an absolutely constant value. At first a saturated potassium chloride electrode (*J*) was used as a check on the

$0.10N$ potassium chloride electrode G . This was useful in that it gave an accurate check on the correctness of the temperature of the bath. A rise of 0.10° in the temperature of the two electrodes increases the difference of potential by 0.05 millivolt.

Throughout these measurements the *E.M.F.* of the cell

(Pt. | H_2 , "standard acetate solution" | saturated KCl | $0.10N$ -KCl, Hg_2Cl_2 , H_2) was repeatedly determined as a check on the "standard acetate," the hydrogen electrodes themselves, and the $0.10N$ -calomel electrode G . With hydrogen electrodes satisfying the conditions described, the value obtained was uniformly 0.6046 ± 0.0001 volt, indicating that the calomel electrode G gave a constant potential differing by perhaps 0.10 millivolt from the mean value given by the four control electrodes alluded to in the preceding paper.

One factor contributed largely to the accuracy of these measurements, namely, the hot, dry weather experienced. This made possible excellent insulation of the whole of the electrical apparatus. On the other hand, before measuring out definite volumes of solution it was necessary to cool the solutions used to 15° . The bath was kept at 18° by means of a rotary pump driven by a turbine. This drew water from the bottom of the bath, and after passing it in turn through a lead coil immersed in ice and water, a heating spiral, and a toluene gas regulator, returned it to the top again. The stream was sufficient in volume to ensure efficient stirring of the bath.

The N acetic acid solutions were prepared as described in the preceding paper. Both the first and last samples from the N acetic acid bottle were titrated against a carefully guarded N -hydrochloric acid solution by means of $0.20N$ -barium with a discrepancy of only 1 in 1000 between the two results.

The N sodium acetate solution was adjusted by the electrometric method previously described. The results of the experiments show that given pure sodium acetate and pure acetic acid, "standard acetate" solution may be readily produced with such accuracy that, in spite of its small diffusion potential and the consequent small time-change of that potential, no differences in composition of two samples can be detected by the most searching hydrogen potential measurements possible in the present state of our knowledge.

All solutions were made up with water of less than 5 ohm-m specific conductivity. For the great majority of these determinations the result would not have been affected if the highest grade "conductivity" water had been used instead.

The contact potential measurements were made by the method described in the preceding paper.

The Change of the Hydrogen Potential of Acetic Acid on Dilution.

In the table below the results of these measurements are given. The first column contains the volume of solution in litres containing 60.03 grams of acetic acid for each dilution examined.

TABLE I.

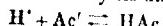
$v \text{ l.c.}$	$E.M.F.$	$d.$	$(E.M.F. - d)_1$	k_1
4	0.49005	0.0003	0.48975	0.00000
5	0.49300	0.0002	0.49280	-0.00007
10	0.50240	0.0002	0.50220	-0.00022
20	0.51115	0.0001	0.51105	+0.00019
35	0.51395	0.0001	0.51385	+0.00037
40	0.52040	0.0001	0.52030	+0.00019
50	0.52350	0.0001	0.52340	-0.00007
100	0.53282	0.0001	0.53273	0.00000
200	0.55105	0.0001	0.55095	-0.00028
300	0.55430	0.0001	0.55420	0.00000
399			(0.56347)	(17.0.10^-6)

The electromotive forces of the cells

Pt | H_2 , acetic acid solution | 4·10*N*-KCl, 0·10*N*-KCl, Hg_2Cl_2 | Hg are given in column 2. In column 3 are the diffusion potential differences (d) against 4·10*N*-potassium chloride solution. They were determined in the manner described, and although they are undoubtedly very small and their inaccuracy affects to no appreciable extent the conclusions which can be drawn from these observations, they resemble all other measurements of contact potential in that they cannot be accepted without a certain reservation. When the values of $(E.M.F. - d)_1$ were plotted against $\log v$ on squared paper it was seen that they approximated very closely to a straight line. This line could be represented by the formula:

$$\log v - 0.60206 = 32.53 \dots \quad (1).$$

In column 5 are given the quantities which would have to be added to the observed $E.M.F.$'s to obtain figures for $(E.M.F. - d)_1$ satisfying equation (1). It is seen that with a maximum error of 35 millivolt in one direction and 0·30 millivolt in the other, $E.M.F. - d$, is a linear function of the logarithm of the dilution. Directly from the equation representing the equilibrium between acetic acid and the ions obtained by its dissociation, that is,



* may, since it is a weak electrolyte, write

$$[H^+][Ac'] = k_a[HAc]$$

$$k_a = \frac{[H^+]^2}{C - [H^+]} \dots \quad (2),$$

where $[H']$ and $[Ac']$ are respectively the hydrogen- and acetic concentrations, $[HAc]$ is the concentration of undissociated acetic acid, and C equals the total concentration of acetic acid. The values of $[H']$ can be calculated from the hydrogen potential ($E.M.F. - d$), given in table I, $\epsilon_1 = 0.3377$, and the constant $v(6)$ by the application of the well-known energy equation quoted in the preceding paper. Since C is known, the values of k_1 for different dilutions can be calculated. The results of calculation performed in this manner are given in column 6 of the same table.

It is seen at once that a minute alteration in the value of the $E.M.F.$ will correspond with a large change in the value of k_1 , the dissociation constant of acetic acid. In order to facilitate the examination of these results the alteration in the value of k_1 obtained by altering the $E.M.F.$ 0.10 millivolt is given in column 7. At this point it will be convenient to mention a discrepancy between these results and those of Loomis and Acree (*Amer. Chem. J.*, 1911, **46**, 585) with respect to the $E.M.F.$ of acetic acid. As the mean of several concordant results, 0.4930 may be taken as their value against the 0.10N-calomel electrode for 0.25N acetic acid, the connecting fluid being 4.10N-potassium chloride. This is 3 millivolts higher than the value found by the present author and corresponds with a dissociation constant of 16.7×10^{-5} . The same values for d and ϵ_1 are taken as those used previously by the author. The acetic acid from which the solutions were made was found free from formic acid, and it is suggested that possibly Loomis and Acree's sample contained traces of higher homologous acids, although in view of the care and high order of accuracy with which their measurements were made this attempt at explanation of the discrepancy is put forward with the greatest diffidence.

The Change of Hydrogen Potential of "Standard Acetate" on Dilution.

"Standard acetate" solution is a solution decimal normal with respect to both acetic acid and sodium acetate. The results obtained, proceeding precisely as with acetic acid, are given in table II.

TABLE II.

$v = 1/C$.	$E.M.F.$	d .	$(E.M.F. - d)$.	$\frac{d}{v}$
5	60360	0.00015	60345	0.00
10	60440	0.00015	60445	0.00
25	60585	0.00010	60575	0.04
50	60683	0.00005	60678	0.10
62.5	60735	0.00000	60735	0.00
100	60794	0.00000	60798	0.04
200	60923	0.00000	60923	0.00
500	61100	0.00000	61100	0.00
1000	61223	0.00000	61223	0.00

In column 1 v represents, as before, the volume occupied by 1 gram-molecule of acetic acid; columns 2, 3, and 4 contain data derived in the same way as in the table for dilutions of acetic acid alone.

If the values of $(E.M.F. - d)$ are plotted against $\log v$, a straight line does not result, but a curve, the nature of which may be judged from the figures in column 5. These were calculated from the formula:

$$x = \frac{\log v - \log 5}{262.1} + 0.60345 - (E.M.F. - d) \dots \dots \quad (7)$$

and represent the $E.M.F.$'s in volts which must be added to the $E.M.F.$ observed, to obtain those values which would have been obtained if the function relating $(E.M.F. - d)$ and $\log v$ had been linear, and if the straight line passed through the observed points corresponding with $v=5$ and $v=1000$.

Determination of the Dissociation Constant of Acetic Acid at Different Concentrations, in Terms of the dissociation of Sodium Acetate at the same concentration, and independently of the E.M.F. of any Auxiliary Electrode.

From the $E.M.F.$ of a hypothetical cell made up of two hydrogen electrodes immersed, one in an acetic acid solution and the other in an acetic acid sodium acetate mixture, it is simple to calculate the value of k_a in terms of a . This determination is independent of the $E.M.F.$ of any auxiliary half cell; the only assumptions are the Ostwald energy relationship involving the constants R , F , T , and the law of mass action as applying to acetic acid.

The values of $(E.M.F. - d)_1$ and $(E.M.F. - d)$ in tables I and II need provide data for the $E.M.F.$'s of a number of these hypothetical cells. Any acetic acid solution of hydrogen electrode potential $(E.M.F. - d)_1$ may be considered linked, without contact potential, to any acetic acid-acetate mixture of hydrogen electrode potential $(E.M.F. - d)$ in table II. The $E.M.F.$ of the cells so made is $(E.M.F. - d) - (E.M.F. - d)_1$, and may be written E_2 . With reference to the data in table II we may write:

$$(E.M.F. - d) = 0.3377 + 0.0577 \log \frac{aC}{k_a C} \dots \dots \quad (8)$$

the solutions, being dilutions of "standard acetate," contain acetic acid and sodium acetate in equal concentrations. Similarly, table I:

$$(E.M.F. - d)_1 = 0.3377 + 0.0577 \log \frac{1}{\sqrt{k_a C_1}} \dots \dots \quad (9).$$

Choosing the data from each table so that for each cell considered:

$$C = C_1,$$

$$(E.M.F. - d) - (E.M.F. - d)_1 = E_1 = 0.0577 \log \frac{aC}{\sqrt{k_a} C}$$

or

$$\log k_a = 2 \left(\log aC - \frac{1}{2} \log C - \frac{E_1}{0.0577} \right) \quad \dots \dots \quad (10)$$

Equations 8 and 9 above, however, are not as accurate as it is possible to make them, although if they are improved E_1 is no longer absolutely independent of the value of ϵ_A . The more accurate equations are (see preceding paper):

$$(E.M.F. - d) = 0.3377 + 0.0577 \log \frac{a' C + [H^+]}{k_a(C - [H^+])}$$

$$(E.M.F. - d)_1 = 0.3377 + 0.0577 \log \frac{1}{\sqrt{k_a(C - [H^+])_1}}$$

and in the special case where $C = C_1$,

$$E_1 = 0.0577 \log \left(\frac{\frac{\mu_{(K)}}{\mu_a} C + [H^+]}{k_a(C - [H^+])} \cdot \frac{1}{\sqrt{k_a(C - [H^+])_1}} \right) \quad \dots \dots \quad (11)$$

Now $[H^+]$ and $[H^+]_1$ are comparatively small quantities, and as they are placed in this equation, an error in their determination resulting from a possible incorrectness of ϵ_A will be without effect; so we may substitute the actual values of $[H^+]$ and $[H^+]_1$, calculate in the ordinary way into this equation, and still regard it as a determination of k_a in terms of a , at the same value of v , independent of the exactness of the value of ϵ_A .

The values of k_a obtained, using equation (11), Kohlrausch's conductivity data, as before, ($\mu_a = 76.8$), and the data from tables I and II, are given below:

v	k_a	k_a (Jones)
5	$17.0 \cdot 10^{-6}$	$17.3 \cdot 10^{-6}$
10	$18.4 \cdot 10^{-6}$	$18.2 \cdot 10^{-6}$
25	$18.8 \cdot 10^{-6}$	$18.5 \cdot 10^{-6}$
50	$19.9 \cdot 10^{-6}$	$18.4 \cdot 10^{-6}$
100	$20.8 \cdot 10^{-6}$	$18.3 \cdot 10^{-6}$
500	$19.0 \cdot 10^{-6}$	$18.0 \cdot 10^{-6}$
1000	$18.4 \cdot 10^{-6}$	$18.0 \cdot 10^{-6}$

For comparison, the latest values for the dissociation constant of acetic acid by the conductivity method have been placed in the column (Jones, *Reports Carnegie Institution*, No. 170).

Summary.

The relationship between the hydrogen potential of acetic acid and the logarithm of its dilution is strictly linear. Assuming ϵ_A

the energy relationship holds, and that the law of mass action applies to acetic acid, and taking as data the constants at present accepted, the dissociation constant of acetic acid would appear to fall steadily with dilution.

Determinations of the dissociation constant of acetic acid in terms of the dissociation of sodium acetate have been made by hydrogen potential measurements, in which the accurate knowledge of the *G.M.F.* of no subsidiary half electrode is involved. The figures taken for the dissociation of sodium acetate were calculated in the usual way from Kohlrausch's conductivity measurements. Assuming that they are correct, the values of the dissociation constant of acetic acid obtained in this way show a rise and a subsequent fall with dilution. The same rise and fall has been observed by ones to a less marked extent in the values of k_a obtained by the conductivity method.

In exactly what direction the results obtained in this and the preceding paper can be applied to qualify the present generalisations with regard to the properties of electrolytes in solution is not at once evident. It would appear that the accuracy of the measurements is sufficiently high to make possible an attempt at the analysis of the discrepancies observed when the data for the dissociation of sodium acetate are more firmly established. Taking into account the magnification of the errors of observation in these calculations of k_a it is certain that the difficulties of providing sufficiently accurate data will disappear only when a higher order of accuracy is reached than is at present possible.

The hydrogen potential of "standard acetate" against the calomel electrode has been redetermined. The result obtained is 0·6016 volt with saturated potassium chloride solution interposed between the two halves of the cell; corrected for contact potential it is 0·6045 volt.

I wish to express my obligations to Prof. S. P. L. Sørensen for his helpful suggestions.

WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HEENE HILL, LONDON, S.E.

CCXXXV.—*The Atomic Weight of Mercury.*

By HERBERT BREKTON BAKER AND WALTER HENRY WATSON

RECENT determinations of the atomic weight of mercury carried out by Easley and by Easley and Brann (*J. Amer. Chem. Soc.*, 1909, **31**, 1207; 1910, **32**, 117; 1912, **34**, 137) by the analysis of mercuric chloride and bromide gave as the result of three very concordant series of experiments the value $Hg = 200\cdot63$, and this figure, rounded off to 200·6, appeared in the International Table of Atomic Weights for 1912. This value is considerably higher than that previously given, namely, $Hg = 200$, a value which is very nearly the mean of all the earlier published determinations. The latter, however, varied between such wide limits as 195 (Hardin) and 200·52 (Erdmann and Marchand), so that there would appear to have been much uncertainty as to the exact value of the constant in question.

It therefore seemed desirable to the authors to redetermine its atomic weight by a method as different as possible from those hitherto employed. The method adopted consists in the synthesis of mercuric bromide by the direct action of liquid bromine on the metal, the excess of halogen being removed by a current of pure dry air. It was found, however, impossible to remove the bromine completely at a temperature below that at which volatilisation of the mercuric bromide became apparent. The amount of adsorbed bromine remaining after heating for one to two hours to 70° was therefore subsequently expelled, after weighing the product and separately determined. In no case did this amount to more than 0·006 per cent. of the product, so that a relatively large error in its determination would not seriously affect the final result. Values for the atomic weight of mercury varying from 200·52 to 200·62 were obtained, and as a mean of nine experiments the value $Hg = 200\cdot57$ was deduced.

This result differs little from those of Easley and Brann obtained by methods differing widely from that of the authors. If, however, traces of mercuric bromide had been lost by volatilisation, which seems improbable in view of the precautions taken, the calculated value of the atomic weight would be too high. The point is of interest in view of the fact that while our experiments were in progress a study of the composition of mercuric oxide was published by Taylor and Hullet (*J. physical Chem.*, 1913, **17**, 7). As a result of their experiments, these authors deduce the value $Hg = 200\cdot37 \pm 0\cdot025$, and suggest the need for a further determination of the atomic weight of mercury.

It is proposed to carry out a further series of determinations on the lines described in this paper, the excess of bromine being, however, removed in a vacuum at the ordinary temperature. A preliminary trial has shown that all but traces can be so removed, and the possibility of weighable amounts of mercuric bromide vapour being lost would thus be avoided.

EXPERIMENTAL.

Preparation of Pure Bromine.

This was made from recrystallised potassium bromide by the method described by Scott (T., 1913, **103**, 847). The product was left for two days over pure quicklime, and then twice distilled in an apparatus constructed entirely of Jena glass, the first and last portions of the distillate being rejected. A portion of the bromine used was from a quantity kindly supplied by Dr. Scott.

Preparation of Pure Mercury.

Mercuric chloride was recrystallised first from pure alcohol and then from water. An aqueous solution of the purified salt was then added slowly to excess of a solution (1.10) of sodium hydroxide kept boiling in a large porcelain dish, the ebullition being subsequently continued for about five minutes. The precipitated oxide was collected, washed free from soluble chlorides, and dried. The product was then decomposed by heating in a hard glass tube, and the resulting mercury collected. The metal was purified by taking vigorously for five minutes with dilute nitric acid (5 per cent), washing well, and then distilling five times under a pressure of about 15 mm. in an apparatus of Jena glass (Fig. 1). Except in the last case the distillation was stopped while still a few c.c. remained behind. In the last distillation the mercury completely distilled without leaving any residue whatever.

Synthesis of Mercuric Bromide.

Two forms of apparatus were used. In certain experiments the apparatus used by one of us for the synthesis of telluric bromide (Karrer and Bennett, T., 1907, **91**, 1857) was employed, whilst in the remaining experiments a modified, somewhat simpler form (Fig. 2) was used. In all cases a similar piece of apparatus was used as a counterpoise, and during an experiment both pieces were, far as possible, treated in exactly the same way.

Mercury was weighed into the bulb of the apparatus and covered with bromine. Action was started by gently shaking the two together, and the apparatus left for half an hour. In no case

was the temperature allowed to rise sufficiently to cause escape of bromine vapour from the apparatus. More bromine was then added, and the apparatus left, stoppered, at room temperature for forty-eight hours or longer. Excess of bromine was then removed by a current of air previously passed through a tube packed with glass wool, then over pieces of potassium hydroxide, and finally through a spiral tube filled with concentrated sulphuric acid. When most of the bromine had been removed, the temperature of the lower part of the apparatus was gradually raised in an air-bath to 70—80°, and maintained at that temperature for two hours. The upper part of the apparatus through which the air escaped was outside the air-bath, and did not become heated above 25—30°; no sublimation of mercury bromide was ever observed on this part.

FIG. 1.

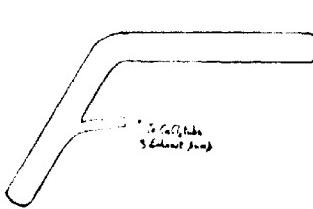
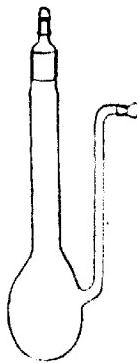


FIG. 2.



The apparatus and mercury bromide were then weighed. In seven experiments more bromine was then added, and after twelve hours the above described treatment repeated, but the change in weight never exceeded a few tenths of a milligram, and was in all probability due to a change in the amount of adsorbed bromine. In all cases the product had a slight pink tint due to free bromine which could only be removed by prolonged heating to a much higher temperature in a current of air or by fusion. As loss of mercuric bromide by volatilisation was to be feared in this case the amount of adsorbed bromine, after drying the product, was determined by slowly heating the bromide to fusion in a current of purified air, which then passed through a solution of potassium iodide. The heating was continued until no further liberation of iodine occurred. The amount of iodine set free was

determined by titration with a $N/100$ -solution of thiosulphate, and never corresponded with more than 0.5 milligram of bromine.

The mercury bromide fused to a clear, slightly yellow liquid, which, when cold, formed a white, crystalline mass, completely soluble in alcohol or hot water. The conversion of the mercury into mercuric bromide appears, therefore, to be complete under the conditions of experiment.

Weighings.

In experiments 1-4 a long-beam Oertling balance was used, and in experiments 5-10 the weighings were made on a short-beam Bunge balance. In both cases the sensibility of the balances was adjusted so that an excess of 0.1 milligram produced a deflexion of 4-5 scale-divisions. Before weighing, the apparatus and its counterpoise were wiped clean with an old silk handkerchief, and left for several hours in a desiccator containing solid potassium hydroxide. They were then transferred to the balance without touching with the fingers, and left for at least an hour before taking the final weighing. The balance cases also contained vessels filled with solid potassium hydroxide.

All the weights given in columns 2 and 3 of the following table have been reduced to vacuum standard by means of the following corrections:

$$\begin{array}{c} -0.000054 \text{ gram per gram of mercury.} \\ +0.000065 \quad " \quad " \quad " \text{ mercuric bromide.} \end{array}$$

Expt.	Wt. of mercury taken.	Wt. of product obtained.	Wt. of adsorbed bromine.	Wt. of combined bromine.	At. Wt. of Br.
1	4.88190	8.77310	(0.00036)	3.89084	200.56
2	6.74796	12.12698	(0.00052)	5.37850	200.54
3	4.79430	8.61672	0.00032	3.82210	200.50
4	4.52480	8.13076	0.00028	3.60568	200.58
5	4.78892	8.60684	0.00050	3.81642	200.57
6	5.52880	9.93452	0.00040	4.40520	200.61
7	4.40148	7.90926	0.00040	3.50738	200.59
8	3.31404		not completed.		
9	4.52338	8.12820	0.00035	3.60450	200.58
10	5.44704	9.78723	0.00040	4.33980	200.62

Mean value (9 experiments). - Hg = 200.57 \pm 0.008.

In Expts. 1 and 2 an attempt was made to determine the adsorbed bromine by dissolving the product in a solution of caesium iodide, but the results were unsatisfactory. The figures given in brackets were therefore calculated on the basis of those obtained in the later experiments.

CCXXXVI.—Adiabatic and Isothermal Compressibilities of Liquids between One and Two Atmospheric Pressure.

By DANIEL TYER.

THE present paper constitutes an extension of a previous one (*J. 1913, 103, 1675*) on the compressibility of liquids, in which a new and precise method for the determination of compressibilities at low pressures was described.

Since the publication of the previous results, it was discovered that a small correction to the observed values had been overlooked. This was due to neglecting the small change in pressure on the liquid caused by the change of level of the liquid in the vertical capillary tube (see the previous paper). Although this pressure is very small compared with the total external pressure change, it introduces a correction greater than the general experimental error and must therefore be taken into account. Fortunately, the correction can be accurately calculated from the observed data and, on the average, causes the results to be raised by about 1 per cent. All the previously obtained results have accordingly been corrected, and the corrected values are contained in the tables in this paper. The necessity of this correction is to be regarded as a disadvantage of the piezometer. It has also been noticed that for rather viscous liquids, such as aniline, the capillary tube requires a long time to drain, and for easily vapourised liquids such as ether, slight errors are introduced by the evaporation of a little liquid in the capillary tube during an experiment. To avoid these disadvantages and sources of error, the piezometer was modified, as is fully described below. In order to test the accuracy of the previous results (corrected as explained above), a few of the determinations were repeated, in each case with the new piezometer. As will be seen from the following tables, the differences between the old and new results are, in general, very small, which gives considerable confidence in the validity and precision of the method.

In order to determine the isothermal compressibility from the adiabatic value, use is made of the following thermodynamic equation:

$$\beta = \alpha + \frac{T \left(\frac{dv}{dt} \right)^{\frac{1}{2}}}{J_e C_p}$$

where β and α are the isothermal and adiabatic compressibilities;

respectively, v the specific volume, J the mechanical equivalent of heat, C_p the specific heat at constant pressure, and T is the absolute temperature.

In the previous work, in order to obtain values of dv/dt and of ϵ , the results of other investigators were relied on. In the case of C_p , errors, even moderately large, have a comparatively small effect on the accuracy of β , but in the case of dv/dt the effect of errors is considerable. It was found that in many cases the values of dv/dt which had been calculated from the specific-volume data of various investigators contained considerable errors, and it was therefore necessary to make a series of accurate specific-volume determinations for each liquid, from which accurate values of dv/dt could be calculated. The practical part of the work is therefore divided into two parts, namely, the determination of adiabatic compressibilities at different temperatures and the determination of specific volumes.

Apparatus: The New Form of Piezometer.

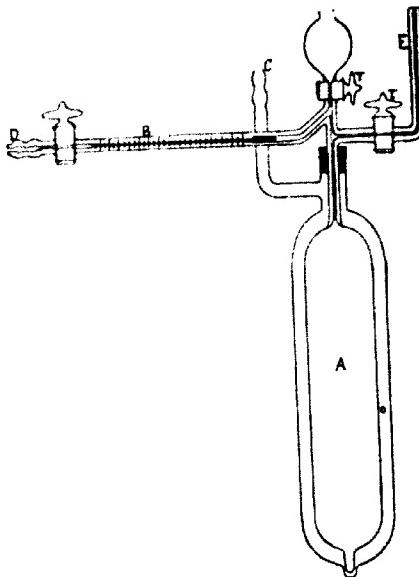
The construction of the piezometer can best be understood by referring to the diagram. The liquid to be investigated is contained in the inner vessel, A , of ordinary soda-glass, filled completely up to and between the two taps, T and T_1 , and the mercury thread in the horizontal capillary tube, B . The two tubes C and D are attached by stout rubber tubing to a small air pump and manometer. On increasing the pressure, the mercury thread is pressed in the graduated tube, B . When the temperature is constant, the pressure is released, and the change in position of the mercury thread in B is noted. The filling of the piezometer is effected by first exhausting it of air, by attaching the side-tube to a strong pump, and then allowing the liquid to enter through tap T . When almost filled, the capillary tube B is dried, the mercury thread allowed to enter, and then the last few c.c. of air expelled from the apparatus by warming. It is emptied by inverting the instrument and attaching the tube E to a suitable exhausted receptacle.

For further details of the rest of apparatus, and the manner of working, the previous paper must be consulted. No correction has been made for the compressibility of the glass is necessary. For the compressibility of the glass, the result of Amagat (2.18×10^{-6}) has been taken as correct.

The volume of the piezometer used was about 450 c.c., and the length of the graduated capillary tube depended on the compressibility of the liquid in the apparatus, but was such as to give

a change of reading of about 6 to 10 cm. for a pressure change of about one atmosphere.

The average error of the adiabatic compressibility determinations does not appear to be greater than 0·1 per cent. Probably the greatest constant error lies in the correction for the compressibility of the glass, but this must be comparatively small, for it was shown in the previous communication that results obtained with a copper piezometer, which requires a much smaller correction than glass,



are in good agreement with the results obtained with a copper piezometer.

Determination of Values of dv/dt .

In order to be able to calculate accurate values for the function dv/dt , very accurate specific volume data--carried out to three decimal places at least--are necessary. The dilatometer is not capable of giving such a degree of accuracy, and hence the *Pyknometer* method of the pyknometer had to be used. The ordinary Spreng-

form of pyknometer is liable to considerable error for volatile liquids, owing to evaporation in the two capillary tubes, and for caustic liquids there is always an appreciable quantity of liquid which clings to the sides of the unfilled part of the capillary tube. A new form of pyknometer was therefore devised which has only one capillary tube instead of two. On the capillary tube is etched a fine mark, and the open end is widened out and provided with a ground-glass stopper. The instrument had an approximate volume of 70 c.c. The empty part of the instrument above the mark on the capillary tube can be thoroughly freed of adhering liquid. The filling and emptying of the pyknometer is effected by attaching to it a small dropping funnel provided with a side tube and tap, through which the instrument is exhausted. The liquid is then run in, and fills the pyknometer completely. The liquid does not come into contact with any rubber connexions during the filling, and is always kept in contact with dry air only. The filling under exhaustion also serves to free the liquid from dissolved air.

As the capillary stem of the instrument may be made to any degree of fineness, the adjustment of the volume may be made to a very superlative degree of accuracy. The weighing of the pyknometer was made to 0·1 milligram, and all weights were reduced to a vacuum. The thermostat used consisted of a large 40 litre water-bath provided with a motor-driven stirrer and a thermoregulator; the temperature remained constant to less than 0·01°. It may be said, therefore, that practically all error lay in the temperature reading. For this purpose, a series of finely graduated thermometers was used, capable of being read with accuracy to less than 0·01°, which had been standardised by comparison with the normal hydrogen thermometer. In addition, they were compared with another set of thermometers, and the fixed points (melting and boiling points) were tested, and the melting point of sodium sulphate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, 32·38°; Richards and Wells, *Zeitsch. physikal. Chem.*, 1890, **26**, 690) was carefully determined. At no point was the correction greater than 0·02°. The error of temperature readings was probably not, on the average, greater than 0·01°.

Now for liquids the value of dv/dt of which is less than 0·001, an error in the temperature reading of 0·01° causes an error in the specific volume for a liquid of average density which affects the sixth decimal place only. Hence it is reasonable and logical to calculate the specific volumes to six decimal places. At the higher temperatures the degree of accuracy would be rather less than this, on account of a somewhat greater temperature error.

The volume of the pyknometer was accurately determined at different temperatures by weighing it filled with boiled, distilled water. These calibrations were also repeated, using distilled mercury in place of the water.* The calibrations were repeated various times to see whether the volume of the pyknometer was altering with time, but no change was observed.

The Pure Liquids.

All the liquids used were highly purified. They were generally fractionally distilled or frozen, and, where possible, they were dried over phosphoric oxide. The fractionation was continued until liquid of constant boiling point was obtained, and the density was unchanged by further distillation. In the following table are given the constants (boiling points and densities at 0°) of the pure liquids used, where these had come within the scope of accurate measurement. (Only boiling points below 100° were accurately measured.) The corrections of the boiling points to normal pressure were made by calculating the values of dt/dp from the Clapeyron-Clausius latent heat relation, which is a much more satisfactory method than the use of tables of experimental values of dt/dp , a function extremely difficult to measure with accuracy.

Liquid.	Density at 0°.	Boiling point at 760 mm.
Carbon disulphide.....	1.29304	46.26
Ethyl acetate.....	0.92468	77.15
Ethylene chloride.....	1.28248	83.45
Chloroform.....	1.62649	61.21
Toluene	0.88412	—
Aniline.....	1.03893	—
Nitrobenzene	1.20323 at 20°	—
Xylene.....	0.88161	—
Ethyl bromide	1.49821	38.40
Ethyl iodide	1.98038	72.52
Benzene	0.88946 at 10°	80.28
Ether	0.73639	34.60
Methyl alcohol	0.81040	64.72
Ethyl alcohol	0.80845	78.32
Chlorobenzene	1.12780	—

Adiabatic Compressibilities and Specific Volumes.

In the following tables are given for each liquid the experimental results of the adiabatic compressibilities. For the liquids which had been previously investigated, the values corrected, as explained in the introduction, are given, together with a

* The specific volumes of water given by Thiesen, Scheel, and Dierckes (Landolt-Bornstein, "Tabellen") were used, and for mercury the results of Tamm (*ibid.*).

supplementary values obtained by means of the new form of piezometer.

For each liquid, also, the experimental specific volume data are given, together with the constants in the equation $V_t = V_0 + at + bt^2$. It was exceedingly laborious to find an equation containing four terms on the right-hand side to fit the experimental results for the whole temperature range, and it was better to find two equations of three terms each covering a range of not more than 40° .

In the following table, t° expresses the temperature in degrees centigrade, α is the adiabatic compressibility, and v the specific volume.

Carbon Disulphide.

t°	$\alpha \times 10^6$	t°	v
<i>Old results corrected.</i>			
0-0	52-95	0-0	0.773370
12-77	57-94	11-66	0.783857
12-58	57-74	16-97	0.788768
20-30	60-01	23-74	0.795154
29-21	63-01	30-72	0.801888
33-39	65-49	39-07	0.810144
40-03	69-13		
<i>New results.</i>			
19-83	60-43		
27-18	63-35		
34-02	66-36		

$$v_t = 0.773370 + 0.0008818 t + 0.01510 t^2.$$

Chloroform.

t°	$\alpha \times 10^6$	t°	α	v
<i>Old results corrected.</i>				
0-0	59-30	0-0	0.655097	
14-14	65-91	10-31	0.683408	
20-96	68-89	15-94	0.688131	
29-42	74-00	25-07	0.675942	
30-77	78-20	32-00	0.682088	
44-80	83-11	40-35	0.689044	
54-31	90-65	47-40	0.690278	
<i>New results.</i>				
0-0	58-64	54-60	0.703199	
9-31	62-65			
24-31	70-75			
35-20	77-35			
49-89	87-25			

$$v_t = 0.655097 + 0.079260 (+0.01576 t^\circ) \quad (0 - 30^\circ).$$

$$v_t = 0.680294 + 0.038323(t^\circ - 30) + 0.01945(t^\circ - 30)^2 \quad (30^\circ - 60^\circ).$$

Toluene.

t° .	$a \times 10^4$.	t° .	τ .
Old results corrected.			
Glass piezometer.			
12.42	64.19	0.0	1.131065
16.01	65.85	14.98	1.148860
27.10	71.16	21.17	1.162269
38.74	77.32	26.78	1.168689
50.26	83.81	30.74	1.168689
60.16	90.84	40.00	1.180721
68.56	97.32	50.13	1.191448
84.11	109.8	73.65	1.22494
		79.73	1.23529
Copper piezometer.			
0.0	58.74	79.24	1.22443
12.41	64.10	89.17	1.26660
47.10	82.10		
57.72	89.00		
67.80	96.88		
90.00	115.3		
New results.			
21.50	68.00		
36.43	78.05		
29.42	72.11		
47.27	82.46		

$$\tau_1 = 1.131065 + 0.0011630(t - 40)^2, \quad (0 - 40^{\circ}).$$

$$\tau_2 = 1.19131 + 0.0013918(t - 50) + 0.02834(t - 60). \quad (50 - 60^{\circ}).$$

Benzene.

t° .	$a \times 10^4$.	t° .	
Old results corrected.			
Glass piezometer.			
9.55	61.40	11.92	1.12687
20.38	66.76	14.40	1.13023
30.52	72.35	17.90	1.13506
36.38	75.64	24.42	1.14402
42.76	79.80	47.95	1.17822
49.54	84.92	58.33	1.19402
49.07	84.02	62.30	1.20023
65.40	97.58	72.06	1.21589
Copper piezometer.			
16.15	63.99		
21.91	67.86		
31.33	72.81		
41.30	79.42		
50.29	85.59		
62.97	95.20		
New results.			
15.96	64.10		
32.03	73.24		
54.58	88.56		
64.00	96.45		

$$\tau_1 = 1.124278 + 0.0013508(t - 10) + 0.01860(t - 10)^2.$$

$$\tau_2 = 1.18129 + 0.0015038(t - 50) + 0.03086(t - 50)^2. \quad [50 - 80^{\circ}].$$

Ether.

t° .	$a \times 10^4$	t° .	v_i
Old results corrected. Glass piezometer.			
0-0 114.3 0-0 1.35793			
11-19	129.4	13.29	1.38615
19-54	139.6	23.90	1.41004
25-30	149.5	28.00	1.41963
30-69	158.3		
Copper piezometer.			
14-63	134.5		
21-11	142.8		
27-52	151.3		
New results.			
10-91	128.24		
18-84	138.62		
24-93	149.05		
29-50	167.73		

$$\nu_i = 1.35793 + 0.0020514(t - 0.0542t^2)$$

Ethyl Alcohol.

t° .	$a \times 10^4$	t° .	v_i
Old results corrected.			
0-0 83.92 0-0 1.23998			
15-52	94.45	14.21	1.25868
28-41	102.04	23.98	1.272043
35-28	105.90	39.16	1.293690
43-34	112.36	46.32	1.30459
51-90	118.9	54.01	1.31638
62-05	128.5	62.71	1.33047
72-31	139.6	72.07	1.34631
New results.			
0-0	83.81		
12-64	91.37		
17-82	94.22		
27-50	100.7		
39-62	109.37		
52-65	120.65		
60-02	126.69		
72-50	139.95		

$$\nu_i = 1.23998 + 0.0012909(t - 0.01767t^2)$$

$$\nu_i = 1.2494 + 0.0014749(t - 40) + 0.03958(t - 40) \cdot [40 - 70^2]$$

Carbon Tetrachloride.

t° .	$a \times 10^6$.	t° .	r.
Old results corrected. Glass piezometer.			
0-0	63-38	0-0	0-612869
12-43	69-33	17-41	0-625728
20-77	73-24	37-80	0-641815
29-09	78-38	46-89	0-649243
38-29	83-88	53-76	0-655021
47-10	90-70	62-63	0-662735
57-72	99-28	72-43	0-671625
67-63	106-74		
Copper piezometer.			
16-18	70-72		
27-19	76-98		
38-69	84-23		
60-10	101-65		
New results.			
0-0	63-04		
16-27	71-25		
24-08	75-04		
38-97	84-82		
45-85	89-30		
53-25	95-68		

$$r = 0-612869 + 0-0-71724t + 0-0-1227t^2,$$

$$r_t = 0-643530 + 0-0-81438(t - 40) + 0-0-1507(t - 40)^2. \quad [40-70]$$

Chlorobenzene.

t° .	$a \times 10^6$.	t° .	r.
Old results corrected.			
0-0	49-19	0-0	0-886685
13-40	54-04	24-32	0-907701
24-24	57-54	38-89	0-920830
35-63	61-83	47-94	0-929336
43-97	65-37	60-63	0-941035
52-79	69-59	73-54	0-954282
62-02	74-38		
71-67	78-87		
80-47	83-3		
New results.			
0-0	49-38		
23-78	57-59		
41-20	64-09		

$$r = 0-886685 + 0-0-84104t + 0-0-9506t^2,$$

$$r_t = 0-921848 + 0-0-91897(t - 40) + 0-0-1285(t - 40)^2. \quad [40-80]$$

Methyl Alcohol.

t° .	$a \times 10^6$.	t° .	r.
0-0	88-94	0-0	1-233821
13-65	98-06	11-33	1-250072
15-17	99-18	24-42	1-269533
21-37	102-93	41-65	1-29639
29-65	109-04	55-20	1-31899
30-80	109-70	68-31	1-32430
24-33	105-64		
39-09	115-93		
43-69	120-12		

$$r = 1-233821 + 0-0014089t + 0-0-2240t^2.$$

$$r_t = 1-278104 + 0-0015261(t - 30) + 0-0-3740(t - 30)^2. \quad [30-60]$$

Ethyl Bromide.

<i>C.</i>	$a \times 10^6$	<i>t</i> ^o	<i>v.</i>
0-0	72-99	0-0	0-667463
10-56	79-45	5-17	0-672046
19-17	85-74	10-73	0-675293
25-23	90-80	17-58	0-683562
31-98	96-63	25-42	0-691098
		31-54	0-697345

$$v = 0-667463 + 0-0,874687 + 0-0,2307 t^o.$$

Aniline.

<i>C.</i>	$a \times 10^6$	<i>t</i> ^o	<i>v.</i>
0-0	32-94	0-0	0-962534
10-68	34-54	5-25	0-966739
20-42	36-35	21-89	0-980373
30-38	38-25	30-63	0-987713
39-57	40-25	50-12	1-004489
49-69	42-78	41-85	0-997117
60-04	45-08	62-35	1-018319
73-56	48-88	79-04	1-03074
85-70	52-43	98-95	1-05003
85-80	52-10		

$$v = 0-962534 + 0-0,798977 + 0-0,8005 t^o.$$

$$v = 1-004384 + 0-0,86953 (-50) + 0-0,1288 (t - 50), \quad (50 - 100^o).$$

Ethylene Chloride.

<i>C.</i>	$a \times 10^6$	<i>t</i> ^o	<i>v.</i>
0-0	48-17	0-0	0-779738
10-81	51-95	5-55	0-784571
19-31	55-31	15-41	0-793457
20-51	55-53	21-03	0-798638
30-52	60-08	31-98	0-808902
25-45	57-72	40-13	0-810912
27-23	58-56	50-74	0-827579
39-16	64-16	59-77	0-837043
50-23	69-95	74-98	0-853501
59-79	75-67		
73-60	85-02		

$$v = 0-779738 + 0-0,867797 + 0-0,1459 t^o.$$

$$v = 0-816785 + 0-0,9842 (t - 40) + 0-0,1943 (t - 40), \quad (40 - 80^o).$$

Acetic Acid.

<i>t</i> ^o	$a \times 10^6$	<i>t</i> ^o	<i>v.</i>
18-98	76-10	19-36	0-051801
29-55	81-36	24-07	0-976685
39-51	87-19	29-54	0-982388
39-37	88-73	34-20	0-99737
49-23	93-57	39-57	0-973016
60-50	102-03	49-69	0-98393
77-44	114-00	60-04	0-99551
		73-48	1-01078
		70-11	1-01755
		99-07	1-04250

$$v = 0-952461 + 0-0010266 (t - 20) + 0-0,1212 (t - 20)^o.$$

$$v = 0-99546 + 0-001110 (t - 60) + 0-0,2405 (t - 60)^o, \quad (60 - 100^o).$$

Nitrobenzene.

t°	$a \times 10^6$	t°	c
14.67	37.33	12.93	0.826309
21.10	34.91	21.25	0.831984
30.77	41.10	30.73	0.835538
40.00	43.26	39.10	0.844402
50.13	45.43	49.99	0.852209
60.15	48.41	58.53	0.868420
73.07	52.26		
82.00	54.92		

$$c = 0.826343 + 0.067665(t - 13) + 0.0162(t - 13)^2. \quad [13-60^{\circ}]$$

Ethyl Iodide.

t°	$a \times 10^6$	t°	c
0.0	59.71	0.0	0.504927
12.17	65.01	10.33	0.510881
23.86	70.85	19.15	0.516144
40.85	80.28	39.32	0.525808
52.10	88.08	24.20	0.519172
62.60	95.93	46.45	0.533512
		53.80	0.538464
		62.72	0.54462

$$c = 0.504927 + 0.056522(t - 30) + 0.01072(t^2)$$

$$c = 0.522549 + 0.06295(t - 30) + 0.01114(t - 30)^2. \quad [30-60^{\circ}]$$

m-Xylene.

t°	$a \times 10^6$	t°	c
0.0	57.27	0.0	1.134417
15.10	63.44	18.83	1.155500
21.38	66.49	22.62	1.159677
30.92	71.15 (?)	29.62	1.16868
32.73	71.67	39.37	1.179694
40.59	75.82	50.54	1.193367
49.72	80.75	59.28	1.20438
61.60	88.00	75.92	1.22627
75.83	97.21	78.86	1.23012
		98.86	1.25867

$$c = 1.134417 + 0.0010925(t - 50) + 0.01461(t^2)$$

$$c = 1.192098 + 0.0012402(t - 50) + 0.02002(t - 50)^2. \quad [50-100^{\circ}]$$

Ethyl Acetate.

t°	$a \times 10^6$	t°	c
0.0	70.30	0.0	1.081456
10.28	83.02	18.22	1.10751
21.89	84.81	27.18	1.121117
30.62	91.50	34.05	1.131909
34.13	94.93	41.04	1.143210
40.47	100.34	52.23	1.161950
50.14	109.39	59.93	1.17552
62.35	122.9	73.21	1.19994
62.90	123.6		

$$c = 1.081456 + 0.0013700(t - 40) + 0.03282(t^2)$$

$$c = 1.14154 + 0.016247(t - 40) + 0.04028(t - 40)^2. \quad [40-80^{\circ}]$$

Water.

t°	$a \times 10^8$ Old results corrected.	$a \times 10^8$ New results.
2.40	50.10	49.71
6.45	49.05	48.51
14.12	47.18	46.98
19.37	46.00	45.23
24.42	45.21	45.38
35.75	44.08	42.38
46.95	43.19	42.98
63.51	42.80	42.29
75.33	42.67	42.46
86.75	42.81	42.62
90.22	42.88	42.90
		47.95
		60.65
		73.50
		84.40
		43.69
		43.04
		42.55
		42.57
		43.00

Isothermal Compressibilities and Values of dv/dt .

Values of dv/dt were determined by differentiating the equations given in the foregoing tables. For the wider temperature ranges where two equations were necessary, it was found that there was usually a slight break in the continuity of the dv/dt values at the intermediate point. This break was removed by plotting the points, and then drawing a smoothed curve, from which values of dv/dt were read. In addition, the accuracy of the results was checked by calculating them in another way. The mean value of dv/dt between each pair of succeeding points was determined by subtracting the specific volumes and dividing by the temperature difference. The result was taken to refer to the mean temperature. Then, by plotting a curve of all the values thus obtained, results were obtained at regular temperature intervals, which, in general, agreed excellently with the values obtained from the equations.

From the values of dv/dt and the adiabatic compressibilities, values of the isothermal compressibility β have been calculated by means of the thermodynamic equation given in the introduction. A knowledge of the specific heat at constant pressure (C_p) is also necessary. As already explained, comparatively large errors in the latter quantity affect the calculated values of β but slightly, and the special determinations of specific heats have been made, but results obtained by other investigators have been relied on. For benzene and carbon tetrachloride, the specific heat determinations of Mills and McRae (*J. Physical Chem.*, 1910, **14**, 797; 1911, 5, 34) have been used in the calculations. Schiff's results (London, 1886, **234**, 300; *Zeitsch. physikal. Chem.*, 1887, **1**, 376) were employed in the cases of toluene, *m*-xylene, ethyl acetate,

and chlorobenzene; Regnault's results ("Relations des Expériences" and *Mém. de l'Acad.*, 1862, **26**, 262) for carbon disulphide, ether, ethylene chloride, ethyl iodide, chloroform, and ethyl alcohol. In the case of aniline, Griffith's results (*Phil. Mag.*, 1876, [v], **39**, 47, 143) were used. In a few other cases, the values of $[v]$, **39**, 47, 143 were used. In a few other cases, the values of the specific heats employed in the calculations are the mean value of several observers. These are given in the tables.

Benzene.

t°	$a \times 10^6$	dv/dt	$\beta \times 10^6$
0	56.00	0.001316	81.95
10	61.00	1361	88.45
20	66.32	1387	95.65
30	72.00	1424	103.15
40	78.26	1464	111.41
50	85.12	1509	120.51
60	92.99	1561	130.63
70	101.91	1623	143.16
80	111.5	1694	158.5

Carbon Tetrachloride.

t°	$a \times 10^6$	dv/dt	$\beta \times 10^6$
0	63.25	0.0007200	91.03
10	68.14	7417	98.31
20	73.28	7642	105.96
30	78.85	7884	114.34
40	85.32	8147	123.94
50	92.90	8432	134.97
60	101.20	8743	147.15
70	109.60	9071	159.81

Carbon Disulphide.

t°	$a \times 10^6$	dv/dt	$\beta \times 10^6$
0	63.21	0.0008818	81.44
10	66.79	9120	87.52
20	66.50	9422	93.54
30	64.52	9724	100.55
40	69.08	10026	107.92
50	74.6	1033	116.3

Ether.

t°	$a \times 10^6$	dv/dt	$\beta \times 10^6$
0	114.30	0.002051	152.97
10	127.05	2169	170.31
20	140.85	2268	188.97
30	158.7	2376	211.5
35	169.0	2430	244.7

Ethylene Chloride.

t°	$a \times 10^6$	d_v/d_t	$B \times 10^6$
0	48.23	0.0008678	70.05
10	51.60	.8970	75.15
20	55.42	.9260	80.73
30	59.80	.9560	86.97
40	64.59	.9875	93.75
50	69.78	0.001022	101.20
60	75.80	1.060	109.73
70	82.53	1.100	119.17
80	89.05	1.143	129.60

Aniline.

t°	$a \times 10^6$	d_v/d_t	$B \times 10^6$
0	32.89	0.0007980	41.31
10	34.47	.8120	43.57
20	36.25	.8270	45.86
30	38.20	.8428	48.34
40	40.32	.8595	51.04
50	42.63	.8775	53.95
60	45.18	.8967	57.15
70	47.83	.9180	60.51
80	50.57	.9420	64.07
90	53.45	.9690	67.87

Chlorobenzene.

t°	$a \times 10^6$	d_v/d_t	$B \times 10^6$
0	49.40	0.0008410	67.02
10	52.66	.8600	71.12
20	56.03	.8783	75.23
30	59.69	.8985	79.82
40	63.73	.9200	85.02
50	68.10	.9438	90.42
60	72.88	.9683	96.28
70	78.00	.9938	102.64
80	83.50	0.001019	109.29

Toluene.

t°	$a \times 10^6$	d_v/d_t	$B \times 10^6$
0	58.75	0.001183	70.34
10	63.03	.9200	84.94
20	67.50	.9239	90.80
30	72.45	.9281	97.28
40	78.10	.9328	104.70
50	84.12	.9379	112.76
60	90.80	.9433	121.57
70	98.16	.9490	131.23

Ethyl Iodide.

t°	$a \times 10^6$	d_v/d_t	$B \times 10^6$
0	59.72	0.0006652	86.59
10	64.10	.5868	92.40
20	68.73	.6081	99.53
30	73.87	.6296	107.29
40	79.73	.6516	115.86
50	86.46	.6735	125.40
60	93.80	.6958	135.72
70	101.75	.7186	146.80

Ethyl Acetate.

T°	$a \times 10^6$	$d_{4/0}^{\circ}/d$	$B \times 10^4$
0	70.30	0.001370	96.29
10	76.43	1434	104.95
20	83.41	1500	114.72
30	91.22	1587	125.3
40	99.86	1635	137.0
50	109.25	1708	149.8
60	120.1	1784	164.2
70	133.4	1864	181.4

Chloroform.

T°	$a \times 10^6$	$d_{4/0}^{\circ}/d$	$B \times 10^4$
0	58.54	0.0007940	85.90
10	62.98	8230	92.94
20	68.31	8538	101.15
30	74.10	8863	110.04
40	80.48	9218	119.96
50	87.33	9598	130.74
60	94.70	0.0010005	142.16

m-Xylene.

T°	$a \times 10^6$	$d_{4/0}^{\circ}/d$	$B \times 10^4$
0	57.27	0.0010925	75.39
10	61.40	1121	80.47
20	65.69	1149	85.69
30	70.35	1179	91.38
40	75.48	1210	97.57
50	80.93	1243	103.99
60	87.04	1279	111.56
70	93.40	1316	119.24
80	100.00	1356	127.30

Ethyl Alcohol.

T°	$a \times 10^6$	$d_{4/0}^{\circ}/d$	$B \times 10^4$
0	83.85	0.001288	99.55
10	89.52	1326	108.28
20	95.65	1385	113.07
30	102.20	1413	120.61
40	109.62	1470	129.12
50	117.82	1542	138.75
60	126.65	1624	149.34
70	137.04	1719	161.8
75	142.95	- 1825	168.9

Water

T°	$a \times 10^6$	$d_{4/0}^{\circ}/d$	$B \times 10^4$
0	50.75	- 0.068	50.78
10	48.38	+ 0.088	48.43
20	46.15	+ 0.207	46.45
30	44.52	304	45.20
40	43.60	380	44.69
50	43.02	455	44.62
60	42.70	526	44.89
70	42.60	592	45.44
80	42.76	655	46.31
90	43.05	720	47.43
100	43.35	782	48.63

Ethyl Bromide.

σ	$a \times 10^4$	dr/dt	C_p^*	$\delta \times 10^4$
0	72.99	0.0608747	0.210	109.05
10	79.05	9208	0.213	119.34
20	86.45	9609	0.216	131.18
30	94.84	0.0010129	0.219	144.20
40	103.70	1059	0.223	157.3

* Calculated from results of Regnault (*loc. cit.*) and Battelli (*Ann. E. Acad.* *Per.*, 1867, [v], **16**, i, 243).

Acetic Acid.

σ	$a \times 10^4$	dr/dt	C_p^*	$\delta \times 10^4$
15	72.80	0.001019	0.480	88.71
20	75.73	1029	0.485	91.98
30	81.55	1048	0.494	98.48
40	87.50	1068	0.504	105.10
50	94.10	1093	0.514	112.55
60	101.18	1122	0.523	120.66
70	108.65	1157	0.533	129.37
80	116.30	1200	0.542	138.57

* From results of Schiff, Timofeev, Lucking and others (See Landolt-Bornstein, "Tabellen")

Methyl Alcohol.

σ	$a \times 10^4$	dr/dt	C_p^*	$\delta \times 10^4$
0	88.95	0.001409	0.570	107.59
10	95.30	1451	0.588	114.94
20	101.95	1495	0.606	122.7
30	109.18	1543	0.625	131.0
40	117.02	1599	0.643	140.3
50	125.48	1666	—	—

* From results of Regnault (*loc. cit.*), Kopp (*Z. Ann. Phys. Chem.*, 1845, [ii], **75**, 98), Schlesinger (*Ann. Phys.*, 1891, **112**, 1261) and Walker and Henderson (*Trans. Roy. Soc. Canada*, 1902, [ii], **8**, 105).

Nitrobenzene.

σ	$a \times 10^4$	dr/dt	C_p^*	$\delta \times 10^4$
0	36.40	0.0000730	0.338	44.70
10	38.61	6852	0.345	47.30
20	40.80	6975	0.352	49.98
30	43.22	7097	0.358	52.79
40	45.70	7219	0.365	55.58
50	48.37	7342	—	—
60	50.28	—	—	—

* From results of Regnault (*loc. cit.*) and Schlesinger (*Ann. Phys. Chem.*, 1896, [iii], 12).

Discussion of Results.

As has been stated, the general order of error in the results for adiabatic compressibility is about 0.1 per cent. This is, however, independent of any possible error in the accepted value (Bragg's value) for the compressibility of glass. In any case,

even supposing that this value contains, say, a 10 per cent. error, then the consequent error in the value of the adiabatic compressibility is only 0.3 per cent. in an average case. It is evident, therefore, that very little error can arise from this source. The accuracy of the calculated values of β depends chiefly on the accuracy of the values of a . Errors in the determinations of dv/dt and C_p have little effect on the value of β . For example, a 5 per cent. error in the value of C_p introduces only an error of 1 to 1.5 per cent. in the value of β .

It must be remarked that whilst the observed values of the adiabatic compressibility refer to a mean pressure of about 1 atmosphere, those of dv/dt and of C_p refer to the normal atmospheric pressure. The effect of pressure on the value of a is small, however, that the results may be considered as all referring to the atmospheric pressure, without any appreciable error being made. In none of the experiments was observed a change of a with a change of pressure of about half an atmosphere. It may be claimed, then, that the values of the compressibility obtained by this method for low pressures are far more accurate than those obtained by the direct method, which yields very discordant results on account of the evolution of a very small but important quantity of heat during compression. The effect of this evolution of heat on the results obtained by the direct method will be easily appreciated from what is explained in the note at the end of this paper.

In every case except water the value of both the adiabatic and isothermal compressibility increases with rise of temperature, the increase being the greater for the isothermal compressibility. For water, both compressibilities show minimum values.

The theoretical application of the results obtained in this work are reserved for a future paper.

Note on some Previous Determinations of the Compressibility of Liquids at Low Pressures.

On comparing the compressibility measurements at low pressures with some results of early investigators, it was found that results which were considered by their authors to be isothermal are really adiabatic.

On studying the work of Quincke (*Ann. Phys. Chem.*, 1851, **19**, 401), it was found that, judging from his method of determination, his results could not possibly be isothermal, but were undoubtedly adiabatic. The same was found to be the case in the determinations of Grassi (*Ann. Chim. Phys.*, 1851, **31**, 437), of Amaury and Deschamps (*Compt. rend.*, 1869, **68**, 177).

and of Collodon and Sturm (*Ann. Chim. Phys.*, 1827, [ii], **36**, 113), and of a few other investigators. It is important to point out the true nature of the results of these investigators, because they have always been recorded in tables of physical constants and properties of liquids as isothermal compressibilities (see, for example, Landolt-Börnstein, "Tabellen," 1912).

Their results differed very considerably from the isothermal compressibility determinations of later investigators, a matter which appears to have caused some surprise, although the reason of the discrepancy was apparently never discovered.

When a liquid is compressed by a small pressure—say, by one atmosphere—there occurs a small rise in temperature amounting to a few thousandths of a degree, yet sufficient, if neglected, to cause a difference of 10 to 40 per cent. in the observed isothermal compressibility, and, as can be easily imagined, the elimination of such a small change of temperature is exceedingly difficult.

It can be easily understood, therefore, that early investigators, ignorant of this small change of temperature, and using thermometers scarcely sensitive enough to detect it, would obtain, not isothermal compressibilities which they were attempting to measure, but really adiabatic compressibilities, or, more correctly, the majority of cases, results which lay between the adiabatic and isothermal values.

Quincke's method of investigation was very similar in principle to that described above. He operated at very low pressures, the first he used being, in fact, little more than 50 cm. of mercury. The latent heat liberated in the compression would be so small as to be undetectable, and it is quite impossible that any appreciable quantity of this heat should have disappeared during an experiment. Moreover, he mentions that he worked as quickly as possible, as then better results were obtained. Quincke himself does not appear to have considered the possibility of the liberation of heat during the compression. In the table below, Quincke's results are compared with the adiabatic and isothermal values recorded in this paper. It will be seen that there is quite a close agreement between Quincke's results and the adiabatic values which leaves no room for doubt that Quincke's values are really isothermal.

Stassi (*loc. cit.*) used a similar form of piezometer to that of Quincke, but he worked at higher pressures, up to 8 or 9 atmospheres. At the higher pressures, the heat produced in the compression would be so appreciable that much of it would be lost during the time of an experiment, but at the lower pressures the

compression would be adiabatic, or approximately so. Now, the isothermal compressibility is much greater than the adiabatic. Grassi found, as a consequence, that the compressibility of a liquid increases with the pressure, whereas it really decreases. For instance, it will be seen in the table that for ether, alcohol, and chloroform the compressibility, according to Grassi, is greater at the higher pressures.

It will be noticed that where a comparison with the present author's results at one to two atmospheres is possible, Grassi's results agree quite well with the adiabatic values. It may be concluded, therefore, that for the lower pressures Grassi's results are approximately adiabatic, but at the higher pressures they lie between the adiabatic and the isothermal values.

Amaury and Deschamps (*loc. cit.*) made compressibility measurements between 1 and 10 atmospheres' pressure. For a change of pressure of 10 atmospheres there would be quite an appreciable change of temperature, but as they took minute readings of the volume change and eliminated what they considered to be accidental changes of temperature by plotting the readings against time, and extrapolating to the zero point on the time ordinate, their results would be approximately adiabatic. The pressures in their experiments being higher than correspond with the present results, it is to be expected that their values will be somewhat lower than the new adiabatic values.

From a study of the early experiments of Collodon and Sadi (*Ann. Chim. Phys.*, 1827, [ii], **36**, 113, 225; *Ann. Phys.*, 1828, **12**, 39), it would appear that their results were not affected by the negligence of the latent heat of compression, so that their values are, as it were, partly adiabatic and partly isothermal.

Author	Liquid.	Temperature.	Pressure (atmospheres).	Compressibility		
				Compressibility × 10 ⁶ observed.	Adiabatic compressibility × 10 ⁶	Isothermal compressibility × 10 ⁶
Quincke (<i>loc. cit.</i>)	Water	0.0°	1—1.5	50.30	50.75	50.75
	Carbon disulphide	0.0	1—1.6	53.93	53.21	53.21
		17.0	1—1.5	63.78	59.35	59.35
	Benzene	0.0	1—1.6	59.70	59.00	59.00
		16.78	1—1.7	66.10	64.00	64.00
	Ethyl alcohol	0.0	1—1.5	82.82	83.85	83.85
		17.51	1—1.7	97.45	94.08	94.08
	Ether	0.0	1—1.5	115.57	114.30	114.30
		14.32	1—1.5	134.23	132.6	132.6

Author.	Liquid.	Temperature.	Pressure (atmospheres).	Compressibility			Adiabatic compressibility $\times 10^6$ (Tyrer).	Isothermal compressibility $\times 10^6$ (Tyrer).
				Pressure found to have no influence on the com- pressibility.	$\times 10^6$ observed.	$\times 10^6$		
Grassi <i>et al.</i>	Water	0-0°	50.3	50.73	50.78			
		4-1	49.9	49.77	49.77			
		10-8	48.0	48.20	48.23			
Taubry and Des- tamps	Ether	0.0	131.0					
		0.0	111.0	114.30	152.97			
		14.0	140.0	132.30	177.6			
		13.8	133.0					
		7.3	82.8	87.95	104.6			
Taubry and Des- tamps	Ethyl alcohol	7.3	85.3					
		13.1	90.4	91.35	108.3			
		13.1	99.1					
Taubry and Des- tamps	Chloroform	8.5	62.5	62.23	91.7			
		12.0	64.8	64.00	95.0			
		12.5	76.3					
Taubry and Des- tamps	Carbon disulphide	0.0	1.10	83.5	83.85	99.05		
		15.0	1.10	91.1	92.50	109.5		
		0.0	1.10	109.0	114.30	152.97		
Taubry and Des- tamps	Carbon disulphide	14.0	128.0	132.30	177.6			
		14.0	63.5	58.28	90.1			

The results of other investigators were carried out at sufficiently high pressures to ensure the complete elimination of the heat of compression.

The practical part of the work was carried out in the Physical Chemistry laboratories of the University of Geneva.

THE UNIVERSITY,
MANCHESTER.

XXXVII.—Electromotive Forces in Alcohol. Part V. The Dropping Electrode in Alcoholic Solutions.

By EDGAR NEWBERRY.

REQUIREMENTS of the electromotive forces of concentration cells cause to furnish the most satisfactory method of comparing the thermodynamic potentials of an electrolyte in two dilute solutions in the same solvent, and in earlier papers of this series such applications with calomel and hydrogen electrodes in alcoholic solutions have been dealt with.

A comparison of the thermodynamic potential of an electrolyte

in one solvent with that of the same electrolyte in another solvent cannot at present be made, previous attempts notwithstanding, by any known electrometric method. The use of concentrations containing two different solvents must at present be wholly excluded, as the potential difference at the boundary cannot be determined directly, and cannot even be roughly estimated, as the calculations involved must be based on theoretical assumptions which would have a purely speculative character.

For this reason the work described in the present series of papers (Hardman, Lapworth, and Partington, T., 1911, **99**, 1417, 153; 1912, **101**, 2249; this vol., p. 2302) is being developed along other lines, which it is believed may ultimately converge at a more promising point of attack. It is sufficient at present to indicate that this point is considered to be the determination of the difference in absolute potential of two electrodes, one in any suitable aqueous solution, and the other in any suitable alcohol solution, and for this purpose it is clear that the precise values of the absolute potentials are not required to be known; moreover the matter is greatly simplified if conditions can be devised so that the absolute potentials of the two electrodes in question are identical.

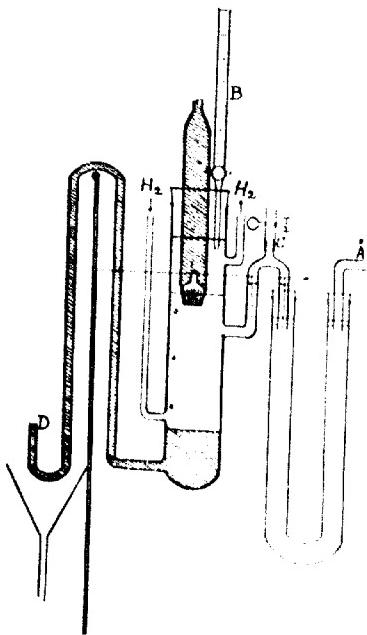
Direct determination of the absolute potentials of electrodes in solutions in both solvents offers one possible line of investigation and of methods hitherto suggested for such determinations as the dropping electrode and the capillary electrometer are the two devices which it is necessary to consider. It is well known that there are great difficulties in reconciling the results obtained by the use of these two instruments even in aqueous solutions, and there are already reasons for supposing that the most rapid progress is likely to be made by further study of the capillary electrometer. The present communication furnishes additional evidence of the untrustworthy character from the present point of view of measurements made with the dropping electrode, even when the results exhibit most perfect consistency, and in later communications it will be shown that the capillary electrometer promises to provide the material necessary for bridging this gap in the application of electrometric methods.

The dropping electrode has been applied to the determination of absolute potentials in aqueous solutions by Paschen (*Ann. Phys. Chem.*, 1890, [iii], **41**, 42) and by Palmaer (*Zeitsch. physik. Chem.*, 1899, **28**, 259; *Zeitsch. Elektrochem.*, 1903, **9**, 151, 371, others).

The apparatus used in the experiments described in the present communication was similar to that used by Palmaer (*Z. physik.*

Elecrochim., 1903, **9**, 755), but with the following modifications:

- (1) Pressure on the mercury was obtained by connecting a large ear-shaped vessel with the mercury dropper by means of 450 cm. of canvas-lined pressure tubing, and raising this vessel when full of mercury by means of a cord passing over a pulley.
- (2) The electrode vessel was arranged so that it could be immersed in a thermostat at 25°.
- (3) A small burette, *B*, holding about 2 c.c., was fitted to the



of the electrode vessel, to allow for the addition of small quantities of any required solution without disturbing the apparatus.

A slow current of pure hydrogen, obtained by the electrolysis of sodium hydroxide solution, was passed through the apparatus for some hours before taking measurements, and continued throughout all the experiments, except in those where hydrogen gas was used.

Potential differences were measured by means of a carefully calibrated metre potentiometer wire, a Weston cadmium cell used as standard, and a sensitive capillary electrometer instrument.

Connexion of the potentiometer with the dropping mercury was made by means of a platinum wire dipping in the mercury in a pear-shaped vessel, and with the still mercury by a platinum wire dipping in the end of the siphon tube *D*.

A is the leading tube of the experimental calomel electrode, the *U* tube below contained the same liquid as the calomel electrode vessel.

With a pressure of 5 atmospheres, 250 c.c. of mercury is twenty-four hours in *N*/10-potassium chloride.

(a) As a preliminary experiment, the absolute *E.M.F.* of the calomel electrode in *N*/10-potassium chloride solution at 25° was determined. In this experiment the following observations were of interest:

(i) Rapid fluctuations of the potential of the still mercury were observed when the potential difference between the dropping and still mercury exceeded 3 or 4 millivolts. These fluctuations were observed by Palmaer only when using hydrogen sulphide in forming his null solution, and were attributed by him to the presence of solid mercury sulphide. Similar fluctuations are, however, observed in many other cases, notably when the single potential of a cathode is measured during electrolysis of a dilute acid. These fluctuations are therefore in all probability due to the lack of balance between the solution pressure of the metal and the osmotic pressure of its ions present in the solution. They may be completely suppressed by the addition of a soluble salt of the metal in question.

(ii) The null solutions used by Palmaer at 18° were found to be unsuitable for use at 25° , a greater proportion of potassium cyanide being required to render the solution null.

In the first experiment 40 c.c. of a solution containing 0.1*N*-potassium chloride, 0.01*N*-potassium cyanide, 0.0005*N*-potassium hydroxide, and 0.0001*N*-mercury cyanide were placed in the electrode vessel, and a similar solution without any mercury was placed in the small burette.

Henderson's equation was employed in this and other cases to determine the diffusion potential due to dissimilarity of the ions in the dropping electrode and calomel electrode vessels respectively. In all cases it was found to be of the order 0.1 millivolt and therefore neglected.

The following table gives the last six readings, where *e* = $E - E_0$

was the burette reading in c.c., II the *E.M.F.* of the calomel electrode against the dropping mercury, and III the difference of potential between the dropping and still mercury:

I	II	III
0.14 c.c.	0.571 volt.	3.2 millivolts
0.21 "	0.575 "	0.8 "
0.25 "	0.579 "	0.6 "
0.29 "	0.582 "	0.0 "
0.33 "	0.584 "	0.6 "
0.48 "	0.611 "	1.6 millivolts

Hence the absolute potential of calomel electrode in $X/10$ potassium chloride solution at 25° is 0.582 volt.

This experiment was carried out three times, giving the values 0.582, and 0.583 volt respectively, the mean result being 0.582 volt.

Assuming the temperature-coefficient of the decinormal calomel electrode to be 0.0008 volt per 1° , this would lead to the value 0.582 volt at 18° , as compared with Palmer's value of 0.574 volt.

Attempts to determine the absolute potential of the calomel electrode in saturated alcoholic salt solution were made, the same apparatus being used, but with the following modifications:

(i) The calomel electrode vessel was specially made with wide long tube and wide-bore tap (1 mm.).

(ii) Connexion between the two electrode vessels was made by filling the liquids into actual contact instead of using moist paper, as was done with aqueous solutions. This was done by using the pinch-tap at *C* and sucking the air out of the joint.

(iii) A delicate Ayrton-Mather reflecting galvanometer was used instead of the capillary electrometer.

The solution in the electrode vessel was 40 c.c. of a saturated solution of pure sodium chloride in pure alcohol (dried over CaH_2), to which was added mercury cyanide until 0.000125 g. was added.

The burette contained a 0.01 N solution of sodium cyanide in water previously saturated with pure sodium chloride.

The following table gives the last five readings, the figures I, II, having the same significance as before:

I	II.	III
0.14 c.c.	0.330 volt	34.0 millivolts
0.32 "	0.330 "	21.4 "
0.54 "	0.331 "	10.6 "
0.68 "	0.331 "	1.0 "
0.77 "	0.331 "	3.4 "

Absolute potential of the calomel electrode in saturated alcoholic potassium chloride solution = 0.331 volt.

A second experiment by the same method gave the same result.
F.L.C.V.

A third experiment, using 0·07*N*-sodium sulphide solution in place of the sodium cyanide, gave 0·329 volt.

A fourth experiment made six months later with a fresh set of solutions similar to those used in the third experiment gave again 0·329 volt. Average of the four results = 0·330 volt.

(c) An attempt was next made to determine the absolute potential of the calomel electrode in saturated aqueous sodium chloride solution.

(i) A saturated solution of pure sodium chloride containing 0·000125*N*-mercury cyanide was placed in the electrode vessel and a similar solution containing 0·1*N*-sodium cyanide in place of the mercury salt was put into the burette.

On adding the solution from the burette until the concentration of the sodium cyanide was two hundred times that of the mercury cyanide, the potential difference between the falling and the still mercury was reduced from 500 to 50 millivolts. Further addition of sodium cyanide produced a still smaller effect, so that it appeared to be impossible to produce a null solution by this method, and was therefore abandoned.

(ii) Palmaer's method of obtaining a null solution by passing gaseous hydrogen sulphide through the liquid was then tried, instead of adding acetic acid to reduce the ionisation of the hydrogen sulphide, it was found necessary to add sodium hydrosulphite to increase it. After making the saturated sodium chloride solution nearly centinormal with respect to sodium hydroxide and passing hydrogen sulphide for eight hours, the potential difference between the dropping and still mercury had only been reduced to 100 millivolts. The figures obtained showed that if a null solution could be obtained by this method it would probably give a value of more than 0·6 volt for the absolute potential of the calomel electrode in saturated aqueous sodium chloride solution. Subsequent experiment showed that this result is undoubtedly too high.

(iii) Sodium sulphide was then tried as the agent for reducing the concentration of the mercury ions, a 0·001*N*-solution of saturated sodium chloride solution being placed in the burette, and 40 c.c. of a saturated sodium chloride solution containing 0·000125*N*-mercury cyanide were placed in the electrode vessel.

A slow current of pure hydrogen was passed through as before. The following table shows the results obtained, the figure 111 having the same significance as before [2(a)ii], whilst column 7 shows the time interval between the readings:

I.	II.	III.	IV.
0.00 c.c.	0.573 volt	504 millivolts.	30 minutes
0.72 "	0.579 "	482 "	30 "
1.44 "	0.586 "	277 "	30 "
1.80 "	0.588 "	250 "	30 "
2.25 "	0.593 "	206 "	21 hours
2.25 "	0.591 "	235 "	30 minutes
2.52 "	0.584 "	230 "	30 "
2.70 "	0.595 "	174 "	30 "
2.83 "	0.593 "	85 "	15 "
2.88 "	0.595 "	60 "	30 "
2.92 "	0.595 "	34 "	15 "
2.92 "	0.593 "	10.6 "	21 hours
2.92 "	0.593 "	238 "	

From this table it will be seen that a null solution is readily attained by the use of sodium sulphide, the potential of the dropping mercury remaining constant whilst the potential of the still mercury altered by 200 millivolts. The addition of sodium sulphide only affected the potential of the dropping mercury to a very small extent when near the null point, although the effect was slightly greater when far away from it.

The effect on the potential of the still mercury was remarkable, although at first it was comparatively small. When near the null point, however, further addition of sodium sulphide, sufficient to increase its concentration by 0.00005M, lowered the potential by more than 100 millivolts, the greater part of which took place within the first ten minutes, reaching the maximum after about three or four hours, and then falling again.

Another remarkable feature of this experiment is the accuracy and certainty with which these results may be reproduced. The experiment was repeated three times, using fresh solutions each time but exactly the same result (0.595 volt) was obtained. By overshooting the mark with excess of sodium sulphide, and subsequently returning to the null point by addition of mercury sulphide, the same result was again obtained. Also, after the series of experiments had been completed, the apparatus was dismantled and laid aside for six months. It was then refitted, new solutions and materials from other sources used, and the above experiment repeated, when exactly the same result was again obtained. Again, from the last line of the above table, it will be seen that by allowing the liquid to remain (with the hydrogen passing at the rate of one bubble per minute) for twenty-one hours, the potential of the still mercury had risen again nearly 250 millivolts. On adding excess sodium sulphide the null point was again reached, and the value in the second column again became 0.595 volt. The actual quantity of sodium sulphide present thus appears to have little or no effect on the potential so long as the null point is attained, and addition can therefore cause no perceptible diffusion potential.

(iv) A similar experiment was carried out with a normal solution of sodium chloride in place of the saturated solution. In this case a greater concentration of sodium sulphide was required to produce the null solution. The fluctuations of potential of the still meter were also greater and more persistent than in the previous case.

Two determinations gave identical results, namely, 0.552 volt, the absolute potential of the calomel electrode in a normal solution of sodium chloride in water.

(v) When a similar experiment was tried with 0.1N aqueous sodium chloride solution, the fluctuations of potential referred to previously were very violent, at times showing a variation of 40 millivolts, and were never entirely absent. Also a high potential E.M.F. appeared to be generated by the dropping mercury, and touching any metallic connexion on the apparatus with the finger or an earthed wire at once gave a large deflexion to the galvanometer, which continued until the earthing body was removed. As the direction of this deflexion was determined by the side of the galvanometer which was touched, it was considered advisable to insulate the whole apparatus on blocks of paraffin-wax before taking further readings.

Three determinations of the absolute potential of the calomel electrode in 0.1N-aqueous sodium chloride solution gave the values 0.534, 0.535, and 0.535 volt respectively.

(vi) It was found possible to produce a null solution in the case of decinormal sodium chloride solutions by the use of sodium cyanide and also by the use of hydrogen sulphide and potassium iodide, although neither of these methods could be used with the stronger solutions of sodium chloride. The use of sodium cyanide gave the following result:

Absolute potential of calomel electrode in $N/10$ sodium chloride solution = 0.579 volt.

The use of hydrogen sulphide and acetic acid gave:

Absolute potential of calomel electrode in $N/10$ -sodium chloride solution = 0.570 volt.

Summary.

The following figures are given by the dropping electrode method of the absolute potentials of the calomel electrode in the solutions given at 25° :

	(a)
In saturated sodium chloride (aqueous)	... 0.595 volt.
" " " (alcoholic)	... 0.329 "
" normal " " (aqueous)	... 0.552 "
" decinormal " " "	... 0.535 "
" " potassium chloride "	... 0.572 "

The figures in column (a) were obtained with the aid of an alkaline sulphate, those in (b) with an alkaline cyanide.

Of these figures, the value given in (b) for $N/10$ -potassium chloride solution at 25° may be taken as approximately correct, as it is nearly the same as that obtained by Palmaer (*loc. cit.*) when corrected for temperature from the known coefficient of the calomel electrode, and is also supported by Smith's observations with the capillary electrometer (*loc. cit.*).

The value given in (b) for $N/10$ sodium chloride solution may also be taken as approximately correct, since it is within three millivolts of that for potassium chloride. A concentration cell with calomel electrodes and $N/10$ solutions of sodium chloride and potassium chloride in opposition showed an *E.M.F.* of about 1 millivolt.

Even a superficial examination of the remaining figures will at once show that they cannot represent true absolute potentials. The potential of the calomel electrode according to these results is greatest in the saturated solution, and least in the most dilute. This is directly contrary to theory, and will be shown later (Part III) to be contrary to fact.

Apparently the use of the alkali sulphide is responsible in part at least for the abnormal results. It was made use of (1) because it was the only substance found that would give a null solution with the stronger aqueous solutions, and (2) because in etholic solution it gave almost the same result as sodium cyanide, which presumably gives true values at least in aqueous solution. Again, the reason why the sodium sulphide produces a null solution with saturated aqueous sodium chloride, when hydrogen fluoride will not, is by no means evident. If it is suggested that it is due to the greater extent of ionisation of the sodium sulphide, it should follow that more sodium sulphide should be required for the saturated sodium chloride solution than in the normal or ethereal, for the sodium sulphide must obviously be less dissolved in the more concentrated sodium chloride solution. This suggestion is not supported by experimental facts, for it was found that the saturated sodium chloride solution required less than half the quantity of sodium sulphide that the normal solution required, and the normal solution required a little less than the decinormal. The foregoing data have been given at some length as they possess so much of definiteness, and therefore must have some real significance which must be considered in any satisfactory vindication of the theory of the dropping electrode, for it will be seen in a future communication that these results, although so

definite, afford no clue to the absolute potential of the $\text{Hg}-\text{Hg}_2^+$ electrode in alcoholic or in concentrated aqueous solution.

The author desires to express his thanks to Professor Lapworth for his encouragement during the progress of the work, and also to acknowledge that some of the apparatus used had been supplied from a grant to Dr. Lapworth from the Government General Research Fund of the Royal Society.

CHEMICAL LABORATORIES,
MANCHESTER UNIVERSITY.

CCXXXVIII. *The Composition of Coal. Part II*

By DAVID TREVOR JONES AND RICHARD VERNON WHEELER

In a previous communication (this vol., p. 140) the result of distilling bituminous coal in a vacuum at a temperature of 430° was recorded. It was noted that there did not appear to be any difference in character between the liquid distillates obtained at that temperature and at 350° . It seemed desirable to examine further the character of the oils obtained at a temperature not exceeding 350° .

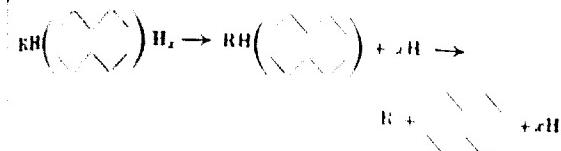
It will be remembered that on distillation at 430° in a vacuum bituminous coals yielded, besides gaseous products and water, about 6.5 per cent. of their weight of tar. On distilling this tar, only half remained as pitch, boiling above 300° . The oil, boiling below 300° , consisted mainly of unsaturated (ethylenic) hydrocarbons, 40 to 45 per cent.; naphthenes (C_8H_{16}) and liquid paraffins, 20 to 25 per cent.; phenols, 12 to 15 per cent.; and aromatic compounds, about 7 per cent.

An examination of the corresponding oils obtained from the distillates from coal in a vacuum at 350° , details of which are given in the experimental part of this paper, showed them to contain the same compounds in similar proportions.

The occurrence of aromatic compounds in the oils obtained at lower temperature requires explanation.

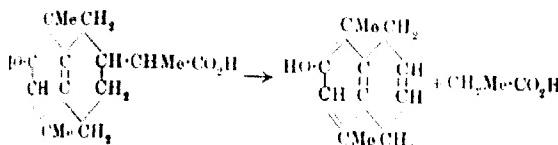
In accordance with a general theory respecting the composition of "coal," put forward to explain the rapid formation of various types of compounds found in coal distillates, the presence in coal was assumed of hydrogenated aromatic nuclei (or $\text{C}_6\text{H}_5\text{H}_2$ molecules), which, it was suggested, suffered decomposition, losing hydrogen, at temperatures not much below 400° —the resulting

perature at which dihydronaphthalene has been found to decompose, thus:

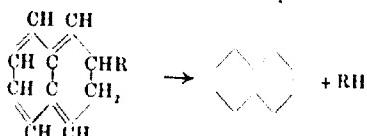


In the light of the results recorded in the present paper, some modification of this theory is required, so far as it affects the aromatic compounds.

The mechanism of decomposition of santonous acid, $\text{C}_{18}\text{H}_{16}\text{O}_3$, as derived by Cannizzaro (*Gazzetta*, 1884, **13**, 385), suggests an alternative. This acid decomposes between 300° and 350° , yielding β -ethyl-1,4-dimethyl-5:8 dihydro β -naphthol and propionic acid, in the following manner:



In an analogous way, the formation of naphthalene derivatives from hydrogenated nuclei in coal can be explained:



According to this decomposition, elimination of hydrogen does not necessarily occur.

Additional evidence of the occurrence of free paraffins in coal, to which reference was made in our previous paper, has been obtained by Kuech and Hibbert (*Mem. Manchester Phil. Soc.*, 1913, **58**, 121), who, in the course of a research on the soluble portions of coal, obtained a paraffin, $\text{C}_{27}\text{H}_{56}$, which they identified with heptane. This paraffin appears to be the same as that described by us as having a molecular weight intermediate between the values quoted for $\text{C}_{26}\text{H}_{54}$ and $\text{C}_{27}\text{H}_{56}$ (*loc. cit.*, pp. 141 and 143).

EXPERIMENTAL.

One and a-half kilos of a Durham bituminous coal, in pieces about 0·3 cm. cube, dried at 105°, were distilled in a vacuum at 350° in the manner described by Burgess and Wheeler (this vol., p. 131). The temperature was maintained without interruption during ten days, at the end of which time gas had practically ceased to be evolved. The coal was allowed to cool, removed from the retort, well stirred, and replaced. Heating as before was then continued during seven days.

The total amounts of tar, oil, and water collected were:

Tar (No. 1 receiver)	13·5 grams
Oil (No. 2 receiver)	6·2 "
Water (No. 2 receiver)	8·3 "

The yield of tar and oils at 350° was thus 1·25 per cent. of the weight of coal used.

The tar in No. 1 receiver had D₄₅ 0·9639. The aqueous layer obtained on washing this tar gave with ferric chloride the same reaction characteristic of o-dihydroxybenzenes, probably hydrocatechol, a substance that has been found by Börnstein to occur in the tars obtained on coking coal at a low temperature.

The oil in No. 2 receiver (which had been kept cool throughout the distillation by a solution of solid carbon dioxide in ether) had D₄₅ 0·8358. This oil was not further examined separately, but was added to the tar in No. 1 receiver. The lower aqueous layer in No. 2 receiver was found to contain hydrochloric acid, as was the case in distillations of the same coal at 430°.

On washing the mixed tar and oils with a solution of sodium hydroxide, their volume decreased by 17 per cent. owing to removal of phenols.

The mixture was washed successively with (1) a dilute solution of sodium hydroxide, (2) dilute sulphuric acid, (3) a solution of sodium carbonate, and (4) water; and, after having been treated with anhydrous magnesium sulphate, was distilled. The composition and specific gravities of successive fractions of the neutral oil are tabulated below:

Fraction.	1.	2.	Residue
Boiling point	170–250°	250–300°	—
D ₄₅	0·8211	0·9066	0·92
Carbon	87·73	88·86	89·49
Hydrogen	12·46	10·71	8·6
Carbon + hydrogen	100·19	99·57	98·17

Fractions 1 and 2 were further examined.

Fraction 1 on being washed with concentrated sulphuric acid suffered a reduction in volume of 44 per cent., due to the removal of olefines. Treatment with fuming nitric acid and weak fuming sulphuric acid effected a further reduction in volume of about 5 per cent., due, for the most part, to the removal of aromatic compounds. The oil remaining, after washing, drying, and distilling from sodium in a vacuum, had the following composition:

Carbon	85.39
Hydrogen	14.93
Carbon + hydrogen ..	100.32

Naphthalenes, (C_8H_{10}), require C = 85.7; H = 14.3 per cent.

Fraction 2, treated in the same manner as fraction 1, suffered a reduction in volume of 56 per cent., due to the removal of olefines, 1 of 6 per cent., due to the removal of aromatic compounds. The residual oil contained:

Carbon	85.44
Hydrogen	14.56
Carbon + hydrogen ..	99.99

The presence of aromatic compounds (naphthalenes) was established by aspirating the vapour from the oils, when heated at 100°, through an aqueous solution of picric acid, when yellow crystals of a salt were deposited.

J. AMPH. L.
CLUMBERLAND.

XXXIX.—Photokinetics of Sodium Hypochlorite Solutions. Part II.

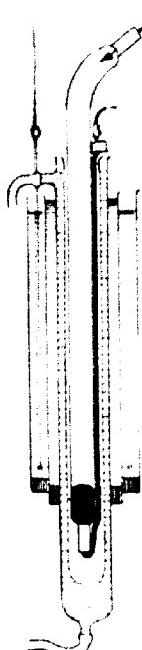
By LEO SPENCER.

The present paper is an account of the continuation of the investigation begun by W. C. McC. Lewis on the photokinetics of sodium hypochlorite solutions (T., 1912, 101, 2371), in which it was shown that the main reaction involved is represented by the equation $\text{NaClO} \rightarrow \text{NaCl} + \text{O}_2$.

For greater convenience and accuracy the method of estimating the hypochlorite was carried out as follows: In order to diminish as far as possible any changes produced by the lowering of the level of the liquid in the reaction space, the amount of liquid titrated was limited to 10 c.c., which made it difficult to estimate the strength of the solution by arsenious oxide and starch-iodide paper. To 10 c.c. of the hypochlorite solution was added 0.02*N*-arsenious

acid in very slight excess, then 0.5 c.c. of a 1 per cent. starch solution, and 1 c.c. of a 10 per cent. solution of potassium iodide, the solution being afterwards titrated with 0.01*N*-iodide. The amount of iodine solution was generally less than 1 c.c.; thus errors due to evaporation of iodine were avoided, and a sharp end-point obtained. With free alkali or acid present, excess of sodium hydrogen carbonate was added, it having been noticed previously

that the end-point was but little affected by either alkali or acid, latter or by sodium carbonate. Duplicate titrations were done at each determination, and the values obtained did not usually differ more than 0.2-0.3 per cent. from each other.



EXPERIMENTAL.

As source of light the same uviolet lamp as was used throughout the work, and all the apparatus, except the outside vessel, was made of uviolet glass (see figure). The lamp was enclosed in a uviolet sheath, which fitted fairly closely to it. This was held by small pieces of cork in a uviolet cylinder (outside diameter 1.96 cm.), drawn out at the bottom into a narrower tube, which served as an inlet for a continuous stream of water, which left through a side-tube at the top, the object of the water stream being to keep the temperature constant. Around this was placed a second uviolet cylinder (outside diameter 7.03 cm.), leaving a space of 0.93 cm. between them for the light filter solution. On the outside of this was the reaction vessel (internal diameter 9.80 cm.), providing a thickness of 1.5 cm. of hypochlorite solution. The bottom of the space was 1.5 cm. above the level of the mercury in the lamp, its height 30 cm. when full. The hypochlorite solution was stirred continually by mechanical means. The solution was kept at 17° C., unless otherwise stated.* The lamp was run off the 230-volt line, in series with a self-induction and resistance; 3.6 amperes were employed as a rule, corresponding with a potential drop of 200 volts across the lamp.

* This approximate constancy in temperature which would be quite inaccurate for ordinary thermal reactions is in the present case sufficient owing to the very small temperature-coefficient (see later).

Preliminary Test.—The first point determined was whether any appreciable disturbance was produced by the level of the liquid falling (due to withdrawals of solution for titration purposes) during the course of an experiment. The rate of decomposition was measured, first with the reaction space full, and then only half full. The result was as follows:

Reaction space full.			Reaction space half full.		
Time	Concentration,	k	Time	Concentration,	k
0	47.69	—	0	47.69	—
0.8	43.63	0.0458	1.0	42.94	0.0455
1.9	39.03	0.0435	2.0	39.05	0.0434
3.0	35.39	0.0432	3.0	35.33	0.0434

The time is measured in hours from the commencement of the experiment. The concentration is that of the sodium hypochlorite expressed in c.c. of 0.05*N*-arsenious acid. k is the unimolecular constant $1/t \log_{10} a/a - r$, where a is the initial concentration of hypochlorite, and $a - r$ is the concentration at time t . When bracketed, thus $[k]$, it represents the unimolecular constant calculated for the interval just preceding the measurement, the end time and concentration being those of the previous reading. $\frac{1}{t_3 - t_2} \log_{10} a - r_2$ for the interval between t_2 and t_3 is:

$$\frac{1}{t_3 - t_2} \log_{10} \frac{a - r_2}{a - r_3}$$

In ordinary circumstances the fall in level did not amount to more than a quarter of the length of the reaction space so comparatively little error could have been introduced from this cause.

Effect of Change of Concentration of the Hypochlorite Solution.

In the previous paper it was found that for the first six hours of the decomposition was fairly well represented by a unimolecular reaction, it being noted, however, that there was a slight tendency for the constant to rise towards the end of that period. The new method of analysis allowed the reaction to be followed over a much greater range of concentration, and as will be seen from the following figures the value began to rise very rapidly as low concentrations were reached.

Time in hours	Concentration in c.c. of 0.02 <i>N</i> -As ₂ O ₃	k	[k]
0.0	30.77	—	—
3.0	21.93	0.0490	0.0490
5.6	16.94	0.0505	0.0522
8.5	10.57	0.0546	0.0627
11.5	6.04	0.0612	0.0810
15.5	1.91	0.0780	0.1250
19.5	0.30	0.1027	0.2010
22.0	0.04	0.1401	0.3500

Effect of Sodium Chloride.

The sodium chloride produced by the decomposition of the hypochlorite might possibly have been responsible for this increase. In order to test this, common salt was added to a quantity of solution until its normality was about four times that of the hypochlorite present. It was found, however, that the velocity under these conditions had actually been slightly decreased. The results were as follows:

Hypochlorite alone 0.08N.			Hypochlorite 0.08N chloride 0.34N		
Time.	Concentration.	<i>k</i>	Time.	Concentration.	<i>k</i>
0.0	44.71		0.0	44.21	
1.0	40.84	0.0393	1.0	40.66	
2.3	35.66	0.0421	2.0	37.39	
4.0	30.34	0.0421	3.5	32.69	

In a parallel experiment the value of the constant was altered from 0.043 to 0.038 by the addition of the same quantity of sodium chloride.

Thus the increase in the constant with time could not have been occasioned by the common salt produced in the reaction.

Absence of Chemical Autocatalytic Effects.

Other products possibly formed in small amounts in the decomposition might have had a tendency to accelerate the decomposition as they accumulated. In order to put this to the test, two series of the same concentration with respect to the hypochlorite were prepared, (a) one by photochemical decomposition of a more concentrated solution, and (b) one by simply diluting with distilled water. If a catalyst were produced in the decomposition itself, it ought to have been present in (a) and absent in (b).

(a)		(b)	
Prepared by decomposition.	Prepared by dilution.	Prepared by decomposition.	Prepared by dilution.
Concentration.	[k]	Concentration.	[k]
21.5	0.059	22.88	
10.6	0.084	11.43	
6.0	0.120	5.47	

The equality in the value of the two rates indicated the absence of autocatalysis, which could not therefore account for the rise in value of the constant. As chemical changes in the reacting system itself appear to be excluded as the cause of the disturbance, it is necessary to ascribe it to alteration in the optical absorption which differs for various parts of the spectrum. This will be considered later.

Effect of Diminishing the Alkali Content.

In the previous paper (Lewis, *loc. cit.*) it was found that the neutralisation of the small amount of alkali present in the solution was followed by an increase in the velocity of decomposition. Further experiments have shown that the addition of a small amount of hydrochloric acid increased the velocity, but that it soon began apparently to fall as more was added. The strength of the sodium hypochlorite solution was usually 0·075*N*; the amounts of sodium carbonate and sodium hydroxide present at the same time were 0·0089*N* and 0·0053*N* respectively. The following table contains the mean velocity constant *k* corresponding with a series of determinations over a time of exposure varying from two to three hours, varying amounts of hydrochloric acid being added at the commencement.

order of experiment	1	2	3	4	5	6
concentration of hydrochloric acid added, expressed in equivalents per litre of the hypochlorite solution	0	0·0091	0·0171	0·0253	0·0379	0·0495
.....	0·0418	0·0510	0·0487	0·0437	0·0304	0·0250

It would appear from the above that the maximum rate is attained when the solution is about neutral. The fact that the greatest normality of the acid added did not exceed 0·05*N* was due to the large amount of chlorine formed, which rendered the titration values unsteady. The first action of the hydrochloric acid is naturally to neutralise the sodium hydroxide present in the solution ordinarily supplied for bleaching purposes. Owing to the weak character of hypochlorous acid the sodium salt will be hydrolysed; the degree of hydrolysis will be much increased by the addition of hydrochloric acid. Apparently, therefore, the undissociated hypochlorous acid molecule is less photosensitive than the ion. Continued addition of hydrochloric acid introduces complications owing to the reaction between hydrochloric and hypochlorous acids.

Effect of Increasing the Alkali Content.

If free alkali was present in the original solution it was desirable to test its action on the decomposition. It was found, however, that sodium hydroxide, even in strength several times that of the hypochlorite, had only a small effect on the reaction. The effect, as it is, represents a diminution in velocity as the alkali increases.

Hypochlorite 0.076 <i>N</i> .			Hypochlorite 0.076 <i>N</i> sodium hydroxide 0.143 <i>N</i>		
Time.	Concentration.	<i>k</i> .	Time.	Concentration.	<i>k</i> .
0.0	47.20	-	0.0	38.26	-
0.5	45.09	0.0396	1.2	34.31	-
1.0	42.98	0.0406	1.7	32.79	-
1.75	39.92	0.0415	2.0	31.84	-
2.25	34.57	0.0416	3.5	27.58	-

In a parallel experiment the value of the constant was determined from 0.0416 to 0.0400 by the addition of 0.358*N*-sodium hydroxide.

Temperature-coefficient of the Reaction.

The temperature-coefficient of the reaction was determined by observations* of the rates at 10° and 24°.

I.	II.	III.	IV.
<i>k</i> at 10°	0.0369	0.0360	0.0373
<i>k</i> at 24°	0.0388	0.0402	0.0397

The mean values give a temperature-coefficient of 1.0% per interval of 10°. This is in agreement with many of the values obtained in other photochemical reactions.

The Effects of Different Spectral Regions.

In the foregoing experiments the light from the lamp was used directly. For quantitative examination, however, it is more important to investigate the effect of separate regions. The action of approximately monochromatic light was studied by employing Winther's light filters (*Ztsch. Elektrochem.*, 1913, **19**, 389), which transmit a known amount of light of a particular wave-length from the uviol lamp whilst absorbing all other lines. Assuming Beer's law to hold for the filters, the concentrations of the constants were so altered that the same amount of light passed through each filter in the present apparatus as passed through the thickness used by Winther. In order to effect this, the concentration of the filter had to be altered in the inverse ratio of the two thicknesses. Since the thickness of the filter layer in the present experiments did not differ by a large amount from that of Winther, this approximation of Beer's law was considered to be justifiable. Winther's measurements were of considerable importance for the present investigation, since they constitute the only quantitative work on the spectrum of the uviol lamp available at the present time. Winther's method is, however, not one of extreme precision.

As a check, two experiments were carried out with wave-lengths in the filter space, one at the beginning of the series, the other

* The temperatures of these measurements were kept constant to 0.05°.

at the end. The respective values were $k = 0.0411$ and 0.0423 , mean 0.0417 . The regions examined corresponded with the lines $\lambda\lambda 436, 405, 366$, and $313 \mu\mu$. The results are as follows:

(458). Plotnikov's filter (isolating the yellow region). Filter transmits 80 per cent. of the line $\lambda 578$ (Plotnikov).

Time in hours.	Concentration in c.c. of As_2O_3 solution.	k .
0.0	35.06	Zero (that is, no appreciable change in concentration).
1.3	35.17	

(459). Winther's filter, transmitting 38 per cent. of line $\lambda 436$.

Time.	Concentration.	k .
0.0	36.40	
1.3	36.01	0.00361
1.8	35.85	366
3.7	35.24	380
4.7	34.96	372
5.6	34.73	0.00465

(460). Winther's filter, transmitting 34 per cent. of line $\lambda 405$.

Time.	Concentration.	k .
0.0	37.81	
1.7	37.21	0.00412
2.3	37.02	0.00400
2.8	36.85	0.00400

(461). Winther's filter, transmitting 27 per cent. of line $\lambda 366$.

Time.	Concentration.	k .
0.0	37.09	
1.6	36.43	0.00482
3.8	35.54	487
5.3	35.05	462
5.9	34.80	0.00469

(462). Winther's filter, transmitting 30 per cent. of line $\lambda 313$.

Time.	Concentration.	k .
0.0	36.46	
1.3	36.23	0.00208
2.3	36.05	213
4.3	35.06	224
4.8	35.00	0.00217

In general, the substitution of approximately monochromatic light in place of the entire spectrum yielded much more consistent values for k . Duplicate experiments were carried out, and agreed closely with those recorded. Mean values of both sets are employed in the summarising table.

The values of the concentrations in the above tables are the mean of three titrations. The results are summarised in the accompanying table:

L.	II. Per cent.	III. Percent.	IV. Percent.	V. Per cent.	VI.	VII.
$\lambda 436 \mu\mu$	35	0.00368	8.8	23.2	1.0	1.6
$\lambda 405$	34	0.00405	9.7	28.5	0.29	4.1
$\lambda 366$	27	0.00475	11.4	41.7	0.25	7.1
$\lambda 313$	30	0.00212	5.1	17.0	0.045	16.1
Complete spectrum	100	0.0417	100			
				Total 110.4		

The wave-length is given in column L. Column II contains Winther's values for the percentage of the line which passes through the light filter. In column III are the values of the unimolecular constants directly observed with the light-filter in position. The last value in this column is the one observed with water only in the filter space. Column IV contains the values of the velocity constants of column III expressed as a percentage of the velocity when water only is present in the filter layer. Column V contains the calculated amount of decomposition, that is, the velocity which would occur if the filter transmitted 100 per cent. of the line and kept back all the others completely. The rate is expressed as a percentage of the rate observed with water alone in the light-filter space. The relative intensities of the lines from the uviolet layer are given in column VI, being taken from the tables given by Winther. Column VII contains the relative rates of decomposition that would be produced if each line were of the same intensity and set free from the rest.

These figures show that the fastest decomposition is effected at the wave-length $\lambda 366$, at the intensity at which it is emitted from the uviolet source. This statement is true not only when the results are calculated (column V) on the basis of 100 per cent. of the line passing through—as actually occurs, of course, when no filter is interposed—but also when no such calculation is made, the direct effect through the filter being measured (column IV). It should be noted, however, that $\lambda 366$ is not the most intense line of the uviolet spectrum (compare column VI). The data in column VII show that if one calculates the velocity constants on the basis of one and the same intensity for all the lines of the spectrum, he obtains the result that the shorter the wave-length the greater the efficiency, that is, $\lambda 313$ is more effective than $\lambda 366$. This is in agreement with the concept of the energy quantum ($h\nu$) and with the photochemical-equivalent law of Einstein, for the shorter the wave-length the greater the frequency, and hence the greater the size of a single quantum. This uniformity in light intensity

however, not the actual state of things in the experiment itself. In the actual case there is a well-marked maximum efficiency at $\lambda 366$, as shown by the figures in column V, due to the simultaneous operation of two effects, namely, the large intensity of this line in the lamp and the large absorbatibility of this region by the solution (the head of the absorption band of sodium hypochlorite lies in the region $290 \mu\mu$). The shortest wave transmitted by the uviolet sheath is $\lambda 320 \mu\mu$ (compare Lewis, *loc. cit.*). As the wave-length increases beyond $\lambda 366$ the efficiency diminishes, so that on reaching $\lambda 578$ (yellow line) and using Plotnikov's filter no chemical effect is observed at all.

Returning to the data of column V it will be noticed that the sum of the effects of the various regions apparently exceeds by a small amount the total value of the lamp as a whole. The most reasonable explanation of this is that the filters not being perfect, certain amount of superposition and repetition of certain parts of the spectrum occurs. The result as it stands favours the view that the effects of different portions of the spectrum are simply additive, a conclusion already come to by Luther and Forbes (*J. Amer. Chem. Soc.*, 1909, **31**, 770).

Owing to the absence of data on the absorption coefficient of sodium hypochlorite solution for the various lines it is not possible at present to compare fully the effect of each line, and thus test Bruner's hypothesis (*Zeitsch. Elektrochem.*, 1913, **19**, 555), to be mentioned in the next paragraph.

Further Discussion of Results.

If a substance in solution obeys Beer's law, and if I_λ denotes the intensity of incident light of wave length λ , c the concentration, b the thickness of the layer, and m is a constant, namely, the absorption coefficient depending only on the substance and wave-length, then the amount of light absorbed will be given by the expression $I_{\lambda 0}(1 - e^{-mb})$. In the paper of Luther and Forbes, referred to, the view has been put forward that the amount of chemical action is proportional to the amount of light absorbed by the solution, and is therefore given by the expression

$$\Sigma k_\lambda I_{\lambda 0}(1 - e^{-mb})$$

Here k_λ is a constant for each wave-length of the incident light. Bruner's hypothesis is equivalent to attributing the same value of k , whatever the wave-length.

From the above "absorption" equation it follows that the effect of dilution on the rate of decomposition will be different according to the amount of absorption that the line undergoes. A line that is almost completely absorbed by a given thickness of, say, a centi-

normal solution will naturally be still more completely absorbed by a decinormal solution. It follows that practically the same amount of optical absorption occurs in the two cases, that is, it is practically complete. If photochemical action depends on the amount of light absorbed, we would expect the same absolute amount of chemical decomposition in the two cases. This is borne out by the following experiments, using the line $\lambda 313$. The mean rate of decomposition of a solution initially $0\cdot075N$ was found to be $0\cdot185$ c.c. per hour (reckoned in terms of the arsenic acid solution). A solution initially $0\cdot013N$ was likewise found to have a mean decomposition value of $0\cdot20$ c.c. per hour, a quantity very nearly the same as the previous, although the absolute concentration in the former case was approximately six times as great as in the latter.

Strictly speaking, there should be no unimolecular constant obtainable in this case, since the law is not $dx/dt = k(a - x)$, but $dx/dt = k$. For purposes of comparison, however, the values of short experiments were used for the calculation of a constant, although it will be clear from the two sets of values that as the decomposition progressed the unimolecular "constant" increased.*

Expt. (a). Initial concentration of sodium hypochlorite $0\cdot075N$ (approx.).

Time in hours.	Concentration in c.c. of As_2O_3 .	Uni. molecular. k .
0·0	36·46	...
1·3	36·23	0·00208
2·3	36·05	213
4·3	35·66	224
4·8	35·60	0·00217

Expt. (b). Initial concentration of sodium hypochlorite $0\cdot013N$ (approx.).

Time in hours.	Concentration in c.c. of As_2O_3 .	Uni. molecular. k .
0·0	6·67	...
1·0	6·46	0·013
1·5	6·37	13
3·5	5·97	0·013

(The k of Expt. (b) indicates the value to which the k of Expt. (a) has risen when the decomposition has proceeded to considerable extent.)

On the other hand, if the amount of the line absorbed is constant, then doubling the concentration will be accompanied by a doubling of the amount of light absorbed, and therefore a doubling of the actual quantity of substance decomposed. In this case the rate of decomposition is proportional to the concentration of the solution, which is expressed by the equation for a unimolecular reaction $dx/dt = k(a - x)$. These conditions were found to be satisfied.

* The comparison mentioned refers to the effects produced by the ether in all cases on solutions initially of approximately the same composition as $0\cdot075N$.

the line $\lambda 405$ (which is only slightly absorbed), as the following results show:

Expt. (c). Initial concentration of sodium hypochlorite = $0.076 N$ (approx.)

Time in hours	Titre.	<i>k</i>
0.0	37.81	—
1.7	37.21	0.00412
2.3	37.02	400
2.5	36.85	0.00400

Expt. (d). Initial concentration of sodium hypochlorite = $0.013 N$ approx.

Time in hours	Titre.	<i>k</i>
0.0	6.71	—
1.5	6.63	0.00347
3.4	6.51	382
4.2	6.46	394
5.1	6.39	0.00412

Although the constant in experiment (d) is not particularly good it is not very different in value from that of experiment (c), that is the constant is independent of the absolute concentration. In experiment (c) the change in the titration value is of the order 15 c.c. per hour as a mean, whilst in (d), the weaker solution, the rate is approximately 0.063 c.c. per hour. A comparison with experiments (a) and (b) illustrates the difference in behaviour in the two cases. These results are in agreement with Luther's "absorption" theory of the velocity of photochemical reactions.

The gradual rise of the unimolecular constant with time observed when water only occupied the filter space is now explicable. The light from the lamp can be considered as made up of two sets of waves, the short wave-lengths which are weak in intensity but are strongly absorbed by the given thickness of solution, and the long wave-lengths of higher intensity, but weakly absorbed by the same thickness of solution. The effect of the long waves is greatest in a strong solution, but rapidly falls off (compare the line $\lambda 405$ above); on the other hand, the effect of the short waves is fairly constant throughout. With both together the long waves are predominant at the outset, and their action is fairly well represented by the unimolecular formula $dx/dt = k(a - x)$. As the solution becomes more dilute, however, the short wave-lengths become more important, with the consequence that the value of the unimolecular "constant" begins to rise since their effect approximates to the effect of the line $\lambda 313$, where $dx/dt = k$ rather than $dx/dt = k(a - x)$ governs the reaction.

Note on the Influence of Light on the Bleaching of Linen by Sodium Hypochlorite.

Two bands of opaque paper were fastened 3 cm. apart round the red lamp, which was enclosed in a uviolet glass sheath. This was immersed in a jar of the hypochlorite solution, and a piece of bleached linen was placed loosely around the lamp. After an

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exposure of one to two hours, the portions of the linen exposed to the rays from the lamp were found to be slightly more bleached than the parts in the shadow. The light had therefore slightly accelerated the bleaching action.

Summary.

(1) The further investigation of the kinetics of the reaction $\text{NaClO} \rightarrow \text{NaCl} + \text{O}_2$, using the mercury uviolet lamp, has been carried out.

(2) By employing Winther's and Plotnikov's filters various spectral regions have been examined and the relative photochemical efficiencies of these regions determined.

(3) The results are in favour of Luther's absorption theory of photochemical action. The general reaction equation may be

$$\frac{dx}{dt} = \sum k_i I_{\lambda_i} (1 - e^{-m\lambda}).$$

For monochromatic light when the absorption-coefficient m is zero the above equation reduces to $dx/dt = \text{constant} \times (a - x)$, that is, apparently unimolecular; when the absorption-coefficient m is large the equation reduces to $dx/dt = \text{constant}$, that is, a "zero-order" equation. These relations have been verified in the case of the lines $\lambda 405$ and $\lambda 313$ respectively.

(4) The temperature-coefficient has been measured, and like the majority of photo-reactions is small.

(5) When the photo-effects are reduced to one and the absolute intensity for the various lines it is shown that the shorter the wave-length the more effective is the decomposition, that is, the greater the velocity constant. Under actual conditions, however, the intensity of the lines differs with the result that $\lambda 365$ is more effective than $\lambda 313$. The latter is the shortest strong line measurable with the uviolet lamp. The head of the absorption band of sodium hypochlorite lies beyond this. Shorter lines will therefore be investigated with the help of quartz apparatus.

(6) It has been found that the presence of light from the mercury lamp slightly accelerates the bleaching of linen by sodium hypochlorite.

In conclusion, the author wishes to express his thanks to Professor W. C. McC. Lewis for suggesting and supervising the research.

THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
THE UNIVERSITY OF LIVERPOOL.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

WHINFIELD,

SALCOMBE,

S. DEVON.

Sept. 18th, 1914.

GENTLEMEN,

I have the honour to forward the Annual Report of the International Committee on Atomic Weights for 1915, which is submitted for publication in the Society's Transactions and Proceedings, as hitherto. Some delay has occurred in presenting it owing to the disturbance of the postal arrangements on the Continent in consequence of the war, and to the illness of Professor Urbain.

The Report deals with all the determinations of atomic weights which have been published since the issue of the preceding Report; & in accordance with the resolution of the Eighth International Congress of Applied Chemistry, no change in the official table of atomic weights will be made until after the meeting of the next Congress. It is recommended, therefore, that the table accompanying the Report for 1913 should be reprinted without alteration.

I have appended the signatures of Professors Ostwald and Planck as desired by them, subject to a qualification by the latter which he proposes to introduce in the French translation of the part in connexion with the atomic weights of Ytterbium and Neptunium.

I am, Gentlemen,

Your obedient Servant,

T. E. THORPE.

The Hon. Secretaries,

The Chemical Society,

London.

Annual Report of the International Committee on Atomic Weights, 1915.

The Council of the International Association of Chemical Societies, with which the Committee on Atomic Weights is now affiliated, recommended, at its meeting in September, 1913, that an annual report of said committee should be published in the *Journal*. The present report, therefore, is submitted in compliance with that recommendation, although delays due to the difficulties

of correspondence may sometimes prevent simultaneous publication in all countries.

Since the report for 1914 was prepared, a number of new atomic weight determinations have been published. These may be briefly summarised as follows:

Silver, Sulphur and Chlorine.—Scheuer (*Arch. Sci. phys.*, 1913, [iv], **36**, 381) dissolved pure silver in sulphuric acid, collected and weighed the sulphur dioxide given off. The weighed sulphate was then converted into chloride by heating in a current of gaseous hydrochloric acid. Three ratios were thus determined which gave the three desired atomic weights, independent of former determinations. The results obtained are Ag = 107.86; S = 32.067; Cl = 35.469. The value for silver is rather high, as other values agree with those generally accepted.

Calcium.—Echsner de Coninck (*Bull. Acad. roy. Belg.*, 1912, 222) has determined the atomic weight of calcium by conversion of the carbonate into the sulphate. His final value is Ca = 40.11.

Barium.—Also redetermined by Echsner de Coninck (*Rev. gén. chim. pure appl.*, 1913, **16**, 245). Barium carbonate was dissolved in nitric acid, and the carbon dioxide so evolved was weighed. The value found was Ba = 137.36.

Copper.—Atomic weight determined by Echsner de Coninck and Ducellez (*Rev. gén. chim. pure appl.*, 1913, **16**, 122). Copper was oxidised by nitric acid, and the oxide was weighed. In the experiments they found Cu = 63.523 to 63.605; in mean, 63.54. These atomic-weight determinations by Echsner de Coninck are published in the briefest possible way, without any of the details that are commonly regarded as essential. How were the substances purified? Were the weights reduced to a vacuum?

Cadmium.—Quinn and Hulett (*J. Physical Chem.*, 1913, **17**, 780) have redetermined the atomic weight of cadmium by electrolysis of the chloride and bromide. In each series the cadmium was collected and weighed in mercury. From the chloride, Cd = 112.45; Cl = 35.458; Cd = 112.32. From the bromide, with Br 1.3% Cd = 112.26. These values agree well with those previously found by Perdue and Hulett, and by Laird and Hulett, but are much lower than the value (Baxter's) adopted in the table. The cause of the difference is yet to be satisfactorily explained, but it may be due to a constant error in one or the other of the methods employed. A change in the table would be premature.

Mercury.—Taylor and Hulett (*J. Physical Chem.*, 1913, **17**, 755) prepared mercuric oxide by heating pure mercury in oxygen. Weighed amounts of the oxide were then decomposed by heating it with metallic iron, and the mercury was collected and weighed.

From the data thus obtained, $Hg = 200.37$. This, as in the case of osmium, is lower than the recognised value, and its acceptance or rejection must await further evidence.

Vanadium.—Atomic weight redetermined by Briscoe and Little (p. 1914, **30**, 64; T., 1914, **105**, 1310) from analyses of the oxychloride, $VOCl_3$. The mean value found was $V = 50.950$ but 50.95 is preferred.

Selenium.—Jannek and Meyer (*Zeitsch. anorg. Chem.*, 1913, **83**, 1), determined the atomic weight of selenium by oxidising Se to SeO_2 . The mean of ten experiments gave $Se = 79.140$.

The same constant was deduced by Bruylants and Bytebier (*Bull. Acad. roy. Belg.*, 1912, 856) from the density of selenium hydride, SeH_2 . In four series of experiments, the weight of a litre of the gas at 0° and 760 mm. was found to be 3.6715 grams. As the weight of a litre of oxygen under the same conditions they find 1.4295 grams.* By the method of limiting densities, and with $H = 1.008$, $Se = 79.18$, which is near the value given in the table.

Tellurium.—Dennis and Anderson (*J. Amer. Chem. Soc.*, 1914, **36**, 882) purified tellurium by preparing the hydride, TeH_2 , from tellurium telluride, and condensing the gas to solid at the temperature of liquid air. From the hydride the metal was obtained by heating to 500° . Thirty-one conversions of Te thus prepared into TeO_2 gave in mean $Te = 127.6$. Other determinations by a volumetric method gave a lower value, near 127.50. The authors conclude that the higher, hypothetical "ditellurium" does not exist.

Scandium.—Lukens (*J. Amer. Chem. Soc.*, 1913, **35**, 1470) prepared scandium oxide from Colorado wolfram. By calcination of sulphate to oxide he found $Sc = 44.59$ and 44.77. The material was probably not quite pure.

Yttrium.—Meyer and Weinheber (*Ber.*, 1913, **46**, 2672), by conversion of yttrium oxide into sulphate, found $Yt = 88.75$. By a reverse process they found $Yt = 88.74$. Corrected to a vacuum, it becomes 88.70.

Ytterbium and Lutecium.—Atomic weights reinvestigated by Peter von Welsbach (*Monatsh.*, 1913, **34**, 1713). For ytterbium (ytterbium metaboranium) he found $Yb = 173.00$. For lutecium (cassiopeium), $Lu = 175.00$.

Iridium.—Holzmann (*Sitzungsher. phys.-med. Soz. Erlangen*, 1914) made four reductions of the salt $(NH_4)_2IrCl_6$ in hydrogen, and found $Ir = 193.42$. This is higher than the accepted value, but not conclusive enough to justify a change.

* According to Germann (*Compt. rend.*, 1913, **157**, 926), the normal litre of oxygen weighs 1.42900 grams.

Helium.—Heuse (*Ber. Deut. physikal. Ges.*, 1913, **15**, 57) has seven determinations of the density of helium, finds the weight of a normal litre to be 0.17856 gram. Hence, by the method of limiting densities, $\text{He} = 4.002$.

Neon.—From two determinations of the density of neon, Letz (*Compt. rend.*, 1914, **158**, 864) finds $\text{Ne} = 20$.

No changes of serious importance seem to be needed in the atomic-weight table. Possibly the values for yttrium, ytterbium, helium, and neon should be changed, but such action may well be deferred until next year. Some experiments by Richards and the (*J. Amer. Chem. Soc.*, 1914, **36**, 819) on the purity of lithium perchlorate also suggest a possible lowering in the atomic weight of silver, namely, from 107.88 to 107.871.

(Signed) F. W. CLEVE
W. OSTWALD
T. E. THORL
G. URBAIN.

NOTE.—Since this report was finished and approved, Professor Urbain has informed us that, jointly with M. Blumenfeld, he has re-determined the atomic weight of neoytterbium with great care. The earth was subjected to many fractionations, and each fraction was studied magnetically and spectroscopically. The value found for the atomic, the mean of thirteen determinations, was 153. He suspects that the "aldebaranium" studied by Auer von Welsbach contained an element of lower atomic weight, probably thulium. Urbain's paper will be published in the near future. F. W. C. T. E. T.

1915.

International Atomic Weights.

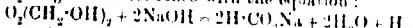
	0 = 16.		0 = 16.
Hafnium	Al 27.1	Molybdenum	Mo 96.0
Hafnium	Sb 120.2	Neodymium	Nd 144.3
Hafnium	A 39.88	Neon	Ne 20.2
Antimony	As 74.96	Nickel	Ni 58.68
Antimony	Ba 187.87	Niton (radium emanation)	Nt 222.4
Antimony	Bi 208.0	Nitrogen	N 14.01
Boron	B 11.0	Osmium	Os 190.9
Bromine	Br 79.92	Oxygen	O 16.00
Cadmium	Cd 112.40	Palladium	Pd 106.7
Cadmium	Cs 182.81	Phosphorus	P 31.04
Cadmium	Ca 40.07	Platinum	Pt 195.2
Cobalt	C 12.00	Potassium	K 39.10
Cobalt	Ce 140.25	Praseodymium	Pr 140.6
Cobalt	Cl 35.44	Radium	Ra 226.4
Cromium	Cr 52.0	Rhodium	Rh 102.9
Cobalt	Co 58.97	Ruthenium	Ru 85.45
Cromium	Cb 93.5	Ruthenium	Ru 101.7
Copper	Cu 63.57	Samarium	Sm 150.4
Dysprosium	Dy 182.5	Scandium	Sc 44.1
Erbium	Er 167.7	Selenium	Se 79.2
Europium	Eu 152.0	Silicon	Si 28.3
Fluorine	F 19.0	Silver	Ag 107.88
Gallium	Gd 157.3	Sodium	Na 23.00
Gallium	Ga 69.9	Strontrium	Sr 87.63
Gallium	Ge 72.5	Sulphur	S 32.07
Gallium	Gl 9.1	Tantalum	Ta 181.5
Gold	Au 197.2	Tellurium	Te 127.5
Helium	He 3.99	Terbium	Tb 159.2
Holmium	Ho 163.5	Thallium	Tl 204.0
Hydrogen	H 1.008	Thorium	Th 232.4
Inert gas	In 114.8	Thulium	Tm 168.5
Iodine	I 126.92	Tin	Sn 119.0
Iridium	Ir 193.1	Titanium	Ti 45.1
Iron	Fe 55.84	Tungsten	W 184.0
Krypton	Kr 82.92	Uranium	U 238.5
Lanthanum	La 139.0	Vanadium	V 51.6
Lead	Pb 207.10	Xenon	Xe 130.2
Lithium	Li 6.94	Ytterbium (Neoytterbium)	Yb 172.0
Lutetium	Lu 174.0	Yttrium	Yt 89.6
Magnesium	Mg 24.32	Zinc	Zn 65.37
Manganese	Mn 54.93	Zirconium	Zr 90.6
Mercury	Hg 200.6		

Organic Chemistry.

Chemistry of Nascent Methylene. E. SGRANIERO (*Gazzetta*, **1914**, *i*, 587—597).—Methyl alcohol reacts violently with phosphoric oxide, and a series of hydrocarbons (cyclic and unsaturated) of the type $(\text{CH}_2)_n$ is formed. Gaseous, liquid and solid members of this series are present, but oxygenated products are absent, as also is cyclohexene.

R. V. S.

Dimethylenediol Peroxide (Diformal Peroxide Hydrate) (J. H. FARROW (*Proc. Roy. Soc.*, 1914, [i], 90, 492—498).—By the separation of approximately equal volumes of concentrated solutions of hydrogen peroxide and formaldehyde at a low temperature in a vacuum over sulphuric acid, a substance, $\text{C}_2\text{H}_6\text{O}_4$, m. p. about 65° , large, triangular plates or prisms, is obtained, which responds only very faintly to tests for hydrogen peroxide and formaldehyde, and is regarded as an “atomic” compound such as *dimethylenediol peroxide*, $(\text{CH}_2=\text{CH})_2$. The substance undergoes little, if any, change in the sun at the ordinary temperature, and dissolves unchanged in water, acetic acid, the solutions giving normal molecular weights by the viscometric method, in the former solution even after forty-eight hours *ad lib.* The crystals explode at about 70° , and take fire in contact with fused iron, platinum black, or warm copper oxide; they are slowly decomposed by exposure to bright sunlight. Treatment of the parent solution of the substance with platinum black causes a rapid decomposition of the potential hydrogen peroxide and a solution of its formaldehyde remains. Aqueous alkalis cause the evolution of a trace of hydrogen in accordance with the equation:



It seems to be no doubt that the compound is identical with that which Fagler, in 1881, obtained amongst the products of slow oxidation of ether.

C. S.

The Lecithin of Egg-Yolk. J. D. RIEDEL (*Chem. Zentr.*, 1914, 196); from *Riedel's Ber.*, 1914, 15—16).—Pure distearyl-lecithin is prepared by extracting lecithin-albumin with light petroleum, and with ether, drying it under reduced pressure, and extracting the substance with methyl alcohol (compare A., 1912, *i*, 744); the oily-alcoholic solution is concentrated under reduced pressure and precipitated with acetone, these operations being repeated a few times. A clear methyl-alcoholic solution is then cooled in a freezing mixture, until to remove phosphatides, and the lecithin in solution is converted into hydrolecithin. This is dissolved in chloroform and methyl acetate is added, when distearyl-lecithin is precipitated as a white mass. It is insoluble in acetone and methyl acetate, soluble in chloroform, sparingly so in cold methyl alcohol, ethyl alcohol, and glycerine, and may be crystallised from its hot ethyl acetate solution.

W. P. S.

Oxidation of Certain Fatty Acids with Branched Chains. HENRY STANLEY RAVER (*Biochem. J.*, 1914, **8**, 320-327).—A scheme of oxidation is suggested by the author which explains the results so far obtained in studying the *katalysis* of α -methylated fatty acids such as α -butyric, α -methylbutyric and α -methylvaleric acid, and also acids, such as γ -methylvaleric acid, which by oxidation at the β -position would yield α -methylated acids. The rule of β -oxidation is applied to these acids with the proviso that the carbon atom of the methyl group which is in the β -position, undergoes oxidation first. The derivative of malonic semialdehyde [formylacetic acid] produced would, by loss of carbon dioxide, give rise to the normal aldehyde, a demethylated fatty acid, and by subsequent oxidation, to the Cannizaro reaction, to the normal acid itself.

In support of this view as a possible biochemical process it is shown that ammonium α -isobutyrate on oxidation with hydrogen peroxide yields amongst other products propaldehyde, and that ammonium α -methylbutyrate yields similarly butaldehyde.

The possibility of this scheme being applied to the katalysis of propionic acid is suggested, since this acid is similarly constituted as regards the position of its methyl group to the α -methylated acids.

H. W. B.

Purification and Melting Points of Saturated Aliphatic Acids. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1914, **11**, 463-467).—Several higher fatty acids have been carefully purified and their melting points redetermined. It has been found that the purest acids after distillation even under very low pressure do not show their maximum melting point. In order to obtain a maximum, several recrystallizations from acetone are required.

Undecenoic acid, prepared by reduction of undecenoic acid and α -hydrogen and palladium, has b. p. 161°/15 mm., m. p. 29-30°. Its amide has m. p. 103°. Lauric acid recrystallized from acetone has m. p. 47.5-48°. Tridecanoic acid, $C_{13}H_{26}O_2$, prepared by oxidation of α -hydroxymyristic acid, has b. p. 202-203°/17 mm., and m. p. 56-57°. Myristic acid has m. p. 57.5-58°. Methyl α -hydroxypalmitate has m. p. 59-60°. Ethyl α -hydroxypalmitate has m. p. 55.5-57°. Pentadecanoic acid, prepared by oxidation of α -hydroxypalmitic acid, has m. p. 53-54°. Palmitic acid has m. p. 63.5-64°. H. W. B.

Preparation and Properties of the Ammonium Salts of Organic Acids. IV. LEROY McMASTER (*J. Amer. Chem. Soc.*, **36**, 1914, 1923).—In earlier papers (Keiser and McMaster, *A. J. C.*, **1**, 248; McMaster, *A. J.*, 444; this vol., **1**, 481) an account has been given of the preparation of the normal ammonium salts of various organic acids by passing ammonia into solutions of the corresponding acids in alcohol or ether. In continuation of this work, the author has prepared normal ammonium *palmitate*, *stearate*, *oleate*, *elaidate*, *acetate*, *salicylate*, *m-hydroxybenzoate*, *p-hydroxybenzoate*, *p-methoxybenzoate*, *β -phenylpropionate*, *hippurate*, *o-toluate*, *phenylacetate*, *mandelate*, and *uridate*. In some of these cases, the salts were prepared by passing ammonia into a solution of the acid in acetone.

E. G.

Cerebronic Acid. IV. The Constitution of Lignoceric Acid. P. A. LEVENS and C. J. WEST (*J. Biol. Chem.*, 1914, **18**, 477–480). Compare A., 1913, i, 889).—The hydrocarbon tetracosane obtained by the reduction of lignoceric acid has m. p. 51–51·5° and has been considered to be identical with n-tetracosane. The latter compound has now been prepared by the action of magnesium on decetyl iodide and found to have m. p. 55°. The hydrocarbon from lignoceric acid must therefore be isotetraicosane, which is in accordance with the views of Meyer (A., 1913, i, 1151).

Decetyl iodide, $C_{12}H_{22}I$, has b. p. 145–150/0·7 mm. It is converted by Grignard's reaction into n-tetracosane, $C_{24}H_{50}$, m. p. 55°, b. p. 21–210°/15 mm.

Ethyl lignocerate is reduced to isotetraacosyl alcohol, $C_{24}H_{48}OH$, b. p. 29/0·8 mm., m. p. 72°. The corresponding isotetraacosyl iodide, $C_{24}H_{48}I$, has m. p. 48°, and by reduction gives n-tetracosane, $C_{24}H_{50}$, melting plates, m. p. 51–51·5°, b. p. 222–225/9 mm. H. W. B.

Clupanodonic Acid. J. D. RIEDEL (*Chem. Zentr.*, 1914, i, 1882; from *Riedel's Ber.*, 1914, 23–27).—The fatty acids obtained by the hydrolysis of brown Japanese sardine oil (iodine number 195) are emulsified in light petroleum, the insoluble bromo-acids are treated in ether, and the residual octabromides, suspended in 96% alcohol, re-treated with zinc dust. Clupanodonic acid, $C_{18}H_{34}O_2$, iodine number 365–370, thereby obtained in 12·7% yield is an oil with a soy odour, which acquires after a time the odour of cod-liver oil, since the acid yields stearic acid and products of lower m. p. by treatment with hydrogen and colloidal palladium; it is probably not an individual substance but a mixture of a derivative of stearic acid and one or more substances, $C_{18}H_{34}O_2$, containing branched chains. C. S.

Ferrie Compounds of Some Hydroxy-acids of the Fatty Series. I. AD. PAIRAS (*Ber.*, 1914, **47**, 1773–1776).—The compounds described are analogous in constitution to the salts of salicylato-ferric acid prepared by Weinland (A., 1913, i, 1189). Potassium ferric glycolato-ferrate, $[Fe(O-CH_2-CO_2)_2]K_2H_2O$, is obtained as an apple-green precipitate when very concentrated solutions of ferric chloride and potassium glycolate are mixed; from diluter solutions the salt is precipitated by means of alcohol. The corresponding sodium salt has m. p. of crystallisation.

When a mixture of ferric hydroxide (1 mol.) and glycollic acid (1 mol.) is kept cold and in the dark for a long time, a micro-crystalline green powder of diglycolato-ferric acid, $[Fe(O-CH_2-CO_2)_2]H_2$, is obtained; it is readily decomposed by water and liberates carbon dioxide from carbonates.

By the addition of sodium carbonate (0·5 mol.) to a solution of ferric oxide (1 mol.) and sodium tartrate (1 mol.), a yellow, sparingly soluble precipitate of tartrato-ferric acid, $(C_4H_2O_6Fe)H_2$, is obtained, which is readily soluble in alkalis; it is also obtained by the interaction of ferric hydroxide and tartaric acid. The sodium and potassium tartrato-ferrates, $(C_4H_2O_6Fe)Na_2H_2O$ and $(C_4H_2O_6Fe)K_2H_2O$, are obtained either from the free acid and the appropriate alkali, or from

ferrie chloride and the alkali tartrates. They are very soluble in water, but can be recrystallised from dilute alcohol. Concentrated solutions, when dried on a glass plate, give large, brownish-yellow scales.

T. S. P.

Thorium Ammonium Oxalate. C. JAMES, C. F. WHITTEMORE and H. C. HOLDEN (*J. Amer. Chem. Soc.*, 1914, **36**, 1853—1858).—Brauner (T., 1898, **73**, 961) has described two thorium ammonium oxalates, $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$ and $2\text{Th}(\text{C}_2\text{O}_4)_2 \cdot (\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$.

A study of the solubility curves of thorium and ammonium oxalate in presence of each other at 25° has now been made, and has indicated that at this temperature only two thorium ammonium oxalates exist (compare Haußer, A., 1912, **1**, 827). E. G.

Cryoscopic Studies on Complexes of Molybdic Acid. I. A. MAZZUCHELLI and C. RANCETTI (*Gazzetta*, 1914, **44**, ii, 116—14; Compare A., 1913, ii, 817).—Cryoscopic and, in some cases, conductivity measurements have been made in order to ascertain the conditions of ionisation and polymerisation of the complexes formed by tartaric, malic, quinic and oxalic acids and their alkali salts with molybdic acid.

The molybdatartaric acids apparently undergo both marked ionisation, the extent of which increases with the content of molybdate trioxide, and also polymerisation, but the degrees to which these changes occur cannot be determined exactly. Comparison of the results obtained with Grossmann and Kramér's polarimetric and conductivity data (A., 1904, **1**, 850) leads to the conclusion that this behaviour is due to association between the anions and the undissociated molecules where there exist in proportions which do not differ greatly. It seems beyond doubt that in very dilute solutions of molybdatartaric acid and in the more concentrated ones of molybdatartaric acids, the molecular weights tend to assume their simple values. Similar behaviour was observed by Pick (A., 1912, ii, 1131) in the case of hydrochloric acid. Analogous relations, although less well defined, hold with the complexes formed by malic acid, but the available data are here less numerous.

Schneider's molybdoquinic acid, $2\text{C}_7\text{H}_{12}\text{O}_6\text{MoO}_5$, and its potassium salt have the simple molecular weights and undergo marked ionisation, which varies considerably with the concentration. Cryoscopic, conductivity and polarimetric measurements render improbable the existence of a second acid of the composition $\text{C}_7\text{H}_{12}\text{O}_6\text{MoO}_4$.

Monomolybdo-oxalic acid, its sodium salt, and also sodium dimolybdo-oxalate have the simple molecular weights and are normally non-ionic. T. P. F.

Synthetic Preparation of *dl*-Glyceraldehyde. E. G. WITZEMANN (*J. Amer. Chem. Soc.*, 1914, **36**, 1908—1916).—A detailed description is given of a method of obtaining crystalline glyceraldehyde in large quantities. The method followed is essentially that of Vell (A., 1898, **1**, 556) and Wohl and Neuberg (A., 1901, **1**, 11), certain modifications are recommended, especially in the manipulation.

of the glyceraldehyde itself, which facilitate the production of the compound and its isolation in a crystalline form.

E. G.

Biochemical Preparation of β -Ethyl Galactoside. EM. BOUZINER and G. MOUREZ (*J. Pharm. Chim.*, 1914, [vii], 10, 157—163. Compare A., 1913, i, 498).—The conditions most suitable for the formation of the galactoside are as follows: Two litres of 80% ethyl alcohol are mixed with 100 grams of galactose and 16 grams of emulsin, and the mixture is kept at 38°; after eight days, a further quantity of emulsin is added, and the action allowed to proceed for a month. The mixture is then filtered, the filtrate is evaporated under reduced pressure, and the excess of galactose destroyed by fermentation with bottom yeast in the presence of dextrose.

β -Ethyl galactoside crystallises in colourless needles, $[\alpha]_D^{20} = 7.21^\circ$, m.p. 161—162°.

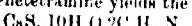
W. P. S.

The Most Appropriate Experimental Conditions for the Preparation of α -Methyl Glucoside and α -Ethyl Glucoside. A. ALESSI (*J. Pharm. Chim.*, 1914, [vii], 10, 202—207. Compare this vol., i, 144).—In the laboratory α -methyl glucoside is best prepared by working with the following proportions of reagents. To 500 grams of methyl alcohol is added a solution of 500 grams of lactose in 4 litres of distilled water, and then 3 litres of a 10% saturation of dried bottom yeast, and the whole is made up to 10 litres. The mixture is allowed to ferment at 18—20° until the rotation of the solution, which to start with is +5°18', has increased to 14°30', i.e. taking about six weeks. The liquid is then neutralised with sodium carbonate, boiled and filtered, and the filtrate distilled to half volume under reduced pressure. The excess of dextrose is destroyed by fermentation with baker's yeast, the liquid again neutralised, boiled and filtered, the filtrate being evaporated to dryness under reduced pressure. From the dry residue, the α -methyl glucoside is treated with alcohol and allowed to crystallise, the yield being 30—200 grams. α -Ethyl glucoside is similarly prepared, using the same proportions, the final purification being carried out by crystallisation from ethyl acetate, and finally from acetone.

W. G.

Calcium Polysulphides. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1914, [v], 23, ii, 8—12).—In investigating the polysulphides of calcium the author has made use of the fixation of labile hydrated salts by means of hexamethylenetetramine (compare Barbieri and Calzolari, A., 1913, i, 181).

The interaction of ammonium pentasulphide and calcium chloride in presence of hexamethylenetetramine yields the compound,



which forms non-hygroscopic, orange-yellow prisms and dissolves in water with partial decomposition and separation of sulphur. Use of a solution of ammonium polysulphide less rich in sulphur results in the formation of the compound, $\text{CaS}_5 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$, which crystallises in large prisms and dissolves in water without apparent alteration.

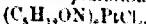
Either of these compounds or a mixture of them is obtainable by the action of hexamethylenetetramine on calcium polysulphide solution prepared from sulphur and either lime or calcium hydrosulphide; the solutions thus obtained may contain calcium polysulphides with low proportions of sulphur, but these would appear to form readily soluble additive compounds with hexamethylenetetramine. T. H. P.

Anhydridification of Glycine. L. BALBIANO (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 893-896).—The assumption made by Massei ("Génèse des Matières protéiques et des Matières humiques. Action de la glycérine et des sucre sur les acides α-aminoïques," Paris) that the action of glycerol on glycine (compare Balbiani and Trasciatti, A., 1914, i, 632; Balbiani, A., 1901, i, 454) is merely that of a dehydrating agent is shown to be inaccurate; when heated with naphthalene or cyclohexane glycine is also converted more or less completely into an anhydride. T. H. P.

New Physiologically Active Derivatives of Choline. ARTHUR JAMES EWINS (*Biochem. J.*, 1914, 8, 366-373).—The following new bases all resemble muscarine in their physiological action, but not one of them is identical with the natural base. *Formylchloride*, $\text{OH}\cdot\text{NMe}_3\text{CH}_2\text{CH}_2\text{O}\cdot\text{CHO}$, is obtained by boiling a solution of choline chloride in formic acid, and isolated in the form of a *platinichloride*, $(\text{C}_8\text{H}_{10}\text{ON})_2\text{PtCl}_6$, orange-red octahedra from water, m. p. 253-256°. The *aurichloride*, $\text{C}_6\text{H}_{11}\text{O}_2\text{N}\cdot\text{AuCl}_4$, forms thin, golden-yellow hexagonal plates, m. p. 175°. *Choline propylchloride*, $\text{OH}\cdot\text{NMe}_3\text{CH}_2\text{CH}_2\text{O}\text{Pr}$, is prepared by acting on β-iodoethyl propyl ether (Karvon, A., 1909, i, 202) with alcoholic trimethylamine solution. The *platinichloride*, $(\text{C}_8\text{H}_{10}\text{ON})_2\text{PtCl}_6$, crystallizes in orange-red prisms, m. p. 246°. *Choline ether*, $\text{O}(\text{CH}_2\text{CH}_2\text{NMe}_3\text{OH})_2$,

prepared by treating ββ-di-iodoethyl ether with a slight excess of alcoholic trimethylamine solution, when the *isotile*, $\text{C}_8\text{H}_{10}\text{ON}_2$, crystallizes in thin, rectangular plates, m. p. 275°. The *chloride* forms rhombic plates, m. p. above 280°. The *platinichloride* crystallizes as clusters of small prisms, m. p. 220° (decomp.); *aurichloride*, pale yellow, rhombic plates, m. p. 269°. *Trimethyl-β-eyanoethylaminomethyl hydroxide*, $\text{OH}\cdot\text{NMe}_3\text{CH}_2\text{CH}_2\text{CN}$, is prepared from β chloro-β-nitro-β trimethylamine. The *chloride*, $\text{C}_8\text{H}_{11}\text{N}_2\text{Cl}$, separates as prisms, 228-229° (decomp.); *platinichloride*, brownish-yellow aggregated octahedra, m. p. 249-250° (decomp.); *aurichloride*, the golden-yellow needles, m. p. 213-214°. *Trimethyl-β-aminoethyl ammonium hydroxide*, $\text{OH}\cdot\text{NMe}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$, is obtained by treating choline nitric acid ester with the calculated amount of ammonia in alcoholic solution. The *aurichloride*, $\text{C}_8\text{H}_{11}\text{N}_2(\text{AuCl}_4)_2$, crystallizes in yellowish-brown, rectangular prisms, m. p. 263°. *N-Bis(β-methoxyaminomethyl) hydroxide*, $\text{OH}\cdot\text{NMe}_3<\text{CH}_2\text{CH}_2\text{O}>$, was prepared by treating dimethylaminomethyl alcohol with one molecular proportion

of ethylene chlorohydrin. The hydroxylamine first produced then loses one molecule of water. The *platinichloride*,



orange-red, rectangular prisms, has m. p. 237—238°; *aurichloride*, $C_5H_{12}ON\cdot AuCl_4$, golden-yellow prisms, m. p. 279°; *mercurichloride*, $C_5H_{12}ON\cdot 2HgCl_2$, hexagonal prisms, m. p. 244—245°.

The following ethers of "formo-choline" [trimethylhydroxy-methylanmonium hydroxide] are prepared by the action of trimethylamine on the corresponding iodomethyl ethers. The *methyl ether*, $OEt\cdot NMe_3\cdot CH_2\cdot OMe$, was analysed in the form of its *iodide*, $C_5H_{12}ONI$, white glistening, hygroscopic plates, m. p. 84°; *platinichloride*, $C_5H_{12}ON\cdot PtCl_6$, orange-red, rhombic prisms, m. p. 234° (decomp.); and *aurichloride*, $C_5H_{12}ON\cdot AuCl_4$, golden-yellow needles, m. p. 13—136°. The *iodide of ethyl ether*, $OEt\cdot CH_2\cdot NMe_3$, thin plates, m. p. 94°; *platinichloride*, orange-red, m. p. 241—242°; *aurichloride*, golden-yellow leaflets, m. p. 138—139°. The *propyl ether* *iodide*, $OPr\cdot CH_2\cdot NMe_3I$, needles, m. p. 108°; *platinichloride*, orange-red needles, m. p. 236—237°; *aurichloride*, golden-yellow leaflets, m. p. 114°. The *butyl ether iodide*, $C_4H_9O\cdot CH_2\cdot NMe_3I$, glistening plates, m. p. 98°; *platinichloride*, orange-red octahedra, m. p. 13—244°; *aurichloride*, golden-yellow leaflets, m. p. 81°.

H. W. B.

Imide of Chlorocamphoric Acid. ANNA MANNESSIER (*Gazzetta*, 1914, 44, i, 697—703). Compare Oddo and Mannessier, A., 1910, i, 399.—When camphorimide is heated for four hours at 120—125° in a sealed tube with phosphorus pentachloride and light petroleum, chlorocamphamide, m. p. 292—293°, is formed, identical with that obtained by Deibler and Knotthe (A., 1912, i, 542) in another way. The substance is very stable; it is not affected by boiling concentrated potassium hydroxide, or by sodium acetate and acetic acid. The *silver salt*, $[H_3O_2NClAg]$, was prepared. The *methyl derivative*, $C_{11}H_{16}O_2NCl$, has prismatic crystals, m. p. 146—147°. The *acetyl derivative* (prepared by the action of acetic anhydride), $C_{11}H_{14}O_2NClAc$, has m. p. 160°, and is very unstable. The *benzoyl derivative* can be prepared only by means of the Grignard reaction; it crystallises in needles, m. p. about 200°.

Bromochlorocamphorimide, $C_{10}H_{18}O_2NClBr$, forms acicular crystals, m. p. 172—174°, and is prepared by the action of bromine on the imide in alkaline, aqueous-alcoholic solution. R. V. S.

Chlorodithiocamphorimide. ANNA MANNESSIER (*Gazzetta*, 1914, 4, i, 703—706). Compare preceding abstract and Oddo and Mannessier, A., 1910, i, 399).—When chlorocamphorimide is heated 200—220° with phosphorus pentasulphide until the evolution of gas ceases, and the mass then extracted with benzene, *chlorodithiocamphor-imide*, $C_{10}H_{14}NS_2Cl$, is obtained; it forms golden-yellow scales, m. p. 135°. When it is boiled for some hours with alkali hydroxide, the solution on acidification deposits a white, amorphous substance, m. p. 4°. Chlorothiocamphorimide dissolves unchanged in concentrated

sulphuric acid, giving a rose-red coloration. When heated at 250° for three hours in a sealed tube with quinoline, it reacts with the substance. On reduction with sodium and alcohol, chlorothiocamphorimide yields camphidine. R. V. S.

The Blue Iron-cyanogen Compounds. H. E. WILLIAMS (*Chem. Met. Min. Soc. S. Africa*, 1914, 15, 1-5).—See P., 1915, 28, 32.

Action of Nitric Acid on Iodoanil. LATHAM CLARKE and F. J. BOLTON (*J. Amer. Chem. Soc.*, 1914, 36, 1899-1908).—By the action of nitric acid on chloranil, Stenhouse (T., 1870, 8, 6) obtained iodopiperin and oxalic acid. It has now been found that the action of nitric acid on iodoanil is quite different; the products in this case are anhydride and di-iodomaleic acid, but neither iodopiperin nor oxalic acid can be detected.

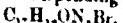
Sodium di-iodomaleate forms small, white plates. The anhydride, $C_2I_2(CO_2H)_2 \cdot NH \cdot Ph$, decomposes at about 152°; when heated in glacial acetic acid it is converted into the *phenylimide*, $C_2I_2(CO_2N) \cdot Ph$, m. p. 171-172°, which crystallizes in small, yellow prisms, and reacts with aniline to form anilinomalephenylimide. In preparing di-iodomalephenylimide, another compound, m. p. 261°, is sometimes obtained which forms small, yellow needles and is probably sodium iodomalephenylimide. When di-iodomaleic acid is heated in *p-toluidine* and glacial acetic acid, *p-toluidinomale-p-tolylimide* is produced. By the action of phenylhydrazine on di-iodomaleic acid the *phenylhydrazone*, $C_2I_2(CO_2N) \cdot NHPh$, m. p. 170°, is obtained together with a smaller quantity of substance, m. p. 226° (decomp.).

When di-iodomaleic acid is heated with water at 160° in a sealed tube, there are obtained carbon dioxide, formaldehyde, hydrochloric acid, little free iodine, and a brown oil from which two white, crystalline substances can be isolated. These substances were not completely investigated, but one of them, m. p. 95-96°, may possibly be di-iodoacetic acid, and the other, m. p. 182-184°, penta-iodoethane. E. G.

Azoinime of *a-Naphthylcarbamic Acid. Action of Grignard Reagent on the Azoinides of Carbamio Acid.* E. CUNIN MANDAI (Gazzetta, 1914, 44, ii, 662-670).—*a-Naphthylcarbamoyl azoinide*, $C_{10}H_7 \cdot NH \cdot CO \cdot N_2$, is obtained by the interaction of a naphthyl carbimide and azoinide (or sodium azoinide and hydrochloric acid) in etheral solution; it forms silky crystals, m. p. 119-120°. When treated with an alcoholic solution of phenylhydrazine, it yields *phenyl-a-naphthylsemicarbazide*, $NHPh \cdot NH \cdot CO \cdot NH \cdot C_9H_7$. This forms silky crystals, m. p. 225-226°. The semicarbazide is oxidized by ferric chloride to the corresponding azo-compound, $C_{10}H_7 \cdot N_2$, which begins to decompose at 170° but melts sharply at 183-184°.

a-Naphthylcarbamoylazoinide reacts with *p-bromophenylhydrazine*, giving *p-bromophenyl-a-naphthylsemicarbazide*, $C_6H_4Br \cdot NH \cdot NH \cdot CO \cdot NH \cdot C_{10}H_7$.

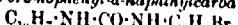
p 230°. On oxidation with ferric chloride, or, better, by the action of nitrous acid, it yields the corresponding azo-derivative,



which forms golden-yellow leaflets, m. p. 163—164°.

On treatment with bromine in benzene solution, 4-bromo-a-naphthyl-carbamoylcarbamide, $\text{C}_{11}\text{H}_9\text{ON}_2\text{Br}$, is obtained; it forms silky needles, *m. p.* 150° (decomp.). When treated with aniline, it yields *p*-bromo-a-naphthylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_8\text{Br}$, which forms needle-shaped crystals, *m. p.* 235° (decomp.). When boiled with alcoholic sodium hydroxide, 4-bromo-a-naphthylcarbamoylazimide yields *p*-bromo-a-naphthylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_{10}\text{H}_8\text{Br})_2$, which crystallises as silky needles, *m. p.* 145—146°.

On boiling *p*-bromoaniline with a-naphthylcarbamoylazimide in alcoholic solution, *p*-bromophenyl-a-naphthylcarbamide,



m. p. 232°, is obtained.

When ethylcarbamoylazimide is subjected to the Grignard reaction with magnesium phenyl bromide, ethylbenzamide, $\text{NHPh}\cdot\text{COPh}$, is produced. Similarly, from phenylcarbamoylazimide, phenylbenzamide is obtained. Phenylcarbamoylazimide and magnesium ethyl iodide yield phenylpropionamide.

R. V. S.

The Question of Priority in Connexion with the Replacement of Alkyloxy by means of Magnesium Alkyl Haloids. EAST SMITH (*Ber.*, 1914, 47, 2260—2261).—A denial of the claim of priority recently advanced by Tschitschibabin and Jelgasin (*this J. C. W.*, 1915).

Study of the Reaction of Alkali Salts of Sulphonic Acids with Alkali Phenoxides by Dry Distillation. ENAAR H. NOLLAU and LEON C. DANIELS (*J. Amer. Chem. Soc.*, 1914, 36, 1885—1891).—The preparation of phenols by the interaction of alkali sulphonates and hydroxides suggested that aromatic ethers should be similarly obtainable from alkali sulphonates and phenoxides. Experiments have therefore been carried out on the dry distillation of alkali sulphonates with alkali phenoxides and have shown that this is a convenient method for preparing aryl ethers of phenols. The yields are smaller than those obtainable by Ullmann and Spiegel's method (*J. 1907*, i, 38), but, in some cases, the compounds used can be more easily prepared. The reaction probably takes place in accordance with the equation: $\text{R}'\text{SO}_3\text{M} + \text{R}''\text{OM} \rightarrow \text{R}''\text{OR} + \text{M}'\text{SO}_3$, in which R' may be the phenyl radicle or one of its homologues, provided that a long side-chain is present, or a methyl group, whilst R'' may be a phenyl or aminophenyl radicle.

The following ethers have been prepared by this method: Diphenyl ether; phenyl *p*-tolyl ether; phenyl *o*-xylyl ether, $\text{C}_6\text{H}_4\text{Me}_2\text{O}\text{Ph}$, *m. p.* 35—37°, b. p. 104—105° (corr.)/49.4 mm., which forms short, colourless needles; *p*-aminodiphenyl ether; phenyl *o*-amino-*p*-tolyl ether, $\text{NH}_2\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\text{Ph}$, b. p. 102—104°/67.4 mm.; phenyl thymyl ether, and anisole.

E. G.

Dibenzylthioresorcinol and Dibenzylthioquinol [1 : 3 and 1 : 4-Dibenzylthiolbenzenes]. Cesare Finzi (*Gazzetta*, 1914, 44, 598–607).—[With Vittorio Fukkotti].—1 : 3-Dibenzylthiolbenzene has m. p. 60° (Zincke and Krüger, A., 1913, i, 45, gave 50°). When an ethereal solution of the substance is treated with bromine, a dibromo-derivative, $C_{20}H_{16}S_2Br_2$, is obtained; it crystallizes in yellow tablets, m. p. 107°. When 1 : 3-dibenzylthiolbenzene is kept in contact with concentrated nitric acid, a mononitro-derivative, $C_{20}H_{15}NO_2$, is obtained; it forms yellow prisms, m. p. 93°.

1 : 4-Dibenzylthiolbenzene, $C_6H_5S(CH_2Ph)_2$, is obtained by condensation of thioquinol with benzyl chloride in the presence of sodium hydroxide. It forms lustrous scales, m. p. 127°. When treated with hydrogen peroxide, potassium dichromate, and acetic acid, or sulfuric acid, it yields the sulphoxide, $C_{20}H_{18}O_2S_2$, m. p. 241°. On treating with hydrogen bromide or hydrogen iodide, the sulphoxide yields 1 : 4-dibenzylthiolbenzene. The sulphone, $C_{20}H_{18}O_4S_2$, is obtained by boiling an acetic acid solution of 1 : 4-dibenzylthiolbenzene with hydrogen peroxide; it becomes brown at 280° and melts at about 31°.

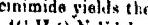
1 : 4-Dibenzylthiolbenzene reacts readily with bromine in chloroform solution, yielding a *perbromide*, $C_{20}H_{18}S_2Br_4$, which is a red, crystalline substance, m. p. 85°. On keeping or on boiling with alcohol, the perbromide loses all its bromine, leaving 1 : 4-dibenzylthiolbenzene. When the perbromide is boiled with water or alkali, however, the sulphoxide, m. p. 241°, is formed.

1 : 4-Dibenzylthiolbenzene periodide, $C_{20}H_{18}S_2I_4$, forms brown crystals, m. p. 120°. It is much more stable than the perbromide. It decomposes very slowly when boiled with water, rapidly when boiled with alkali, but 1 : 4-dibenzylthiolbenzene is formed, not the sulphoxide. The sulphoxide is produced, however, when the periodide is shaken with silver acetate in acetic acid solution. R. V. S.

Periodides of Acid Amides and their Additive Products with Metallic Salts. Substances of Exceptionally High Molecular Weight. F. J. Moore and Ruth M. Thomas (*J. Amer. Chem. Soc.*, 1914, 36, 1928–1937).—In the course of an investigation of benzyl bromoamide (Moore and Cederholm, A., 1906, i, 831), an attempt was made to prepare benzoyliodoamide for comparison by dissolving iodine in an aqueous solution of sodium hydroxide, adding powdered benzyl amide and acidifying with acetic acid. Instead of the desired compound, however, a *periodide*, $3C_6H_5CO\cdot NH_2NaI_3$, was produced, which crystallized in long, slender, green needles. This substance can be readily prepared by heating a mixture of benzamide, sodium iodide, and iodine with water or nitrobenzene. The corresponding *potassium* compound, m. p. 128–130°, was also prepared. A *perbromide* of similar character was obtained from benzamide, potassium bromide, and bromine. Benzamide, potassium bromide, and iodine yield a compound which forms greyish-green needles. Dibenzamide, potassium iodide, and iodine furnish a green substance, resembling the corresponding benzamide compound. The compound, $2C_6H_5CO\cdot NH_2HI_3$, was obtained in the form of flakes with a greenish-black iridescence.

The barium and copper compounds, $6C_6H_5CO\cdot NH_2BaI_4$ and

$C_6H_5CO-NH_2CuI_2$, are described. Cobalt and nickel iodides yield similar products. The compounds, $(3C_6H_5CO-NH_2KI)_n \cdot HgI_2$, p. about 50°, and $(3C_6H_5CO-NH_2KI)_n \cdot PbI_2$, are remarkable for their exceptionally high molecular weight, that of the latter being 60. A crystalline compound of benzamide, mercuric iodide, hydrogen iodide, and iodine was prepared, but was too unstable for analysis. Indications were obtained of the formation of similar periodides from tolanamide, *p*-bromobenzamide, phthalimide, benzenesulphonamide, & various anilides. Succinimide yields the compound,



which has already been described by Pintti (A., 1896, i, 364).

E. G.

Dinitro-*m*-arylsalicylic Acids, Mononitro-*m*-arylsalicylic acids, and *m*-Nitroxanthones, and their Derivatives. ATTILIO RASORI (*Gazzetta*, 1914, 44, i, 641–646).—The *m*-dinitroarylsalicylic (dinitro-*o*-xyloxybenzoic) acids described below are prepared by acting sodium 2-chloro-3:5-dinitrobenzoate with the sodium derivatives of phenols and cresols at a temperature not greater than 140°.
3:5-Dinitro-2-phenoxycybenzoic acid, $OPh-C_6H_3(NO_2)_2-CO_2H$, forms pale blue crystals, m. p. 148°. Its ethyl ether has m. p. 98°.
3:5-Dinitro-2-o-tolylxybenzoic acyl forms pale yellow crystals, p. 130°. Its ethyl ether has m. p. 88°.
3:5-Dinitro-2-m-tolylxybenzoic acid crystallises in yellow needles, p. 164°.
3:5-Dinitro-2-p-tolylxybenzoic acid has m. p. 157.5°.

When 3:5-dinitro-2-phenoxycybenzoic acid is treated with concentrated sulphuric acid on the water-bath, it does not yield the corresponding sulphonate; at a higher temperature (about 150°) it is sulphonated, yielding the sulphonic acid, $SO_3H-C_6H_3-O-C_6H_3(NO_2)_2-CO_2H$, which crystallises in scales, m. p. above 350° (decomp.).

The following acids were obtained from 2-chloro-3-nitrobenzoic acid the same way as those already described, but copper powder must be added as a catalyst and a temperature of 170° is needed.

Nitro-2-phenoxycybenzoic acid forms colourless needles, m. p. 168°.

Nitro-2-o-tolylxybenzoic acid forms colourless leaflets, m. p. 118°. The corresponding *m*- and *p*-acids have m. p. 172° and 174° respectively.

Nitro-2-methylisopropylphenoxycybenzoic acid (from thymol) forms colourless leaflets, m. p. 177°.

Nitro-2-m-hydroxypheenoxybenzoic acid has m. p. 212°.

Nitro-2-phenoxycybenzoic acid when treated with sulphuric acid on water-bath readily yields the corresponding *nitroxanthone*,



which on reduction with ammonium sulphide give the *aminoxanthone*, H_2O_2N , which forms yellow laminae, m. p. 205°, and gives an *acetyl-amine*, $C_{11}H_{11}O_2N$, m. p. 178°. The aminoxanthone can be nitrated. The solution of the diazo-compound on boiling yields *xyanthonone*. The diazo compound gives a yellow precipitate with phenol, and a scarlet precipitate, m. p. 255°, with β -naphthol.

R. V. S.

Sulphosalicylic Acid and its Hexamethylenetetramine Salts. J. D. RIEDEL (*Chem. Zentr.*, 1914, i, 1896—1897; from *Riedel's Ber.* 1914, 17—23).—When crystallised from water and dried below 10°, sulphosalicylic acid contains 2H₂O, and has m. p. 108—110°; the anhydrous acid is obtained by drying the substance at 105° for a long time; it decomposes at about 200°. The ready solubility of sulphosalicylic acid in water does not afford a means of detecting the presence in it of salicylic acid, since the solubility is not affected by quantities of up to 4% of the latter. *Hexal* (primary) and *neohexal* (hexamethylenetetramine sulphosalicylate) each contain 1H₂O. The former decomposes at about 190° and the latter at 180° (compare this vol., i, 45). *Hexal* may be obtained in the anhydrous state by drying under reduced pressure at 100°, but *neohexal* decomposes under these conditions. Anhydrous *neohexal* may, however, be prepared from anhydrous sulphosalicylic acid, hexamethylenetetramine and absolute alcohol; it crystallises in prisms, m. p. 180°. W. P. S.

m- and p-Phenylenedithiolacetic Acids. C. FINZI (*Gazzetta* 1914, 44, i, 579—587).—*m-Phenylenedithiolacetic acid*, C₈H₈(S-CH₂-CO₂H)₂, can be obtained by the condensation of thioresorcinol with chloroacetic acid in alkaline aqueous solution; it crystallises in triclinic prisms, m. p. 132°. The silver salt, C₁₀H₈O₄S₂Ag₂, was prepared. The *aniline salt*, C₈H₈(S-CH₂-CO₂H)₂NH₂Ph, has m. p. 134°. The acid yields a *monobromo-derivative*, C₈H₈Br(S-CH₂-CO₂H)₂,

m. p. 164°. When the acid is oxidised with hydrogen peroxide, corresponding *sulphoxide* and *sulphone* are obtained as white, amorphous substances. Their *silver salts* have the compositions C₁₀H₈O₄S₂Ag₂ and C₁₀H₈O₄S₃Ag₂, respectively.

p-Phenylenedithiolacetic acid, C₈H₈(S-CH₂-CO₂H)₂, is obtained in the condensation of thiorequinol and chloroacetic acid in *water* solution; it crystallises in slightly yellow prisms. The *sodium salt*, C₁₀H₈O₄S₂Na₂, and the *silver salt*, C₁₀H₈O₄S₂Ag₂, were prepared. The *aniline salt*, C₈H₈(S-CH₂-CO₂H)₂·2NH₂Ph, forms long prisms and softens at 123° and are completely melted at 163°. The *sulphoxide* has m. p. 168° (decomp.) and gives a *silver salt*, C₁₀H₈O₄S₃Ag₂. The *sulphone* has m. p. 226° (decomp.) and gives a *silver salt*, C₁₀H₈O₄S₄Ag₂. *p-Phenylenedithiolacetic acid* does not react with bromine.

As thiorequinol is present in all samples of thioreoscorcinol, certain quantities of *p-phenylenedithiolacetic acid* are produced in the preparation of *m-phenylenedithiolacetic acid*; their removal can be effected by carrying out the condensation in particular conditions which are described. R. V. S.

Identity of Hydroxnararingenin with Phloretin. H. HENRY FRANCIS (*Chem. Zentr.*, 1914, ii, 253—254; from *Beitr. Phys.* 179—186).—By the catalytic hydrogenation of nararingenin (*J. T.*, 1910, 97, 2054) in alcoholic solution with palladous chloride and hydrogen, a dihydronararingenin identical with phloretin was obtained.

In vitro acetyl derivative forms prismatic plates, m. p. 96°. When heated with aqueous potassium hydroxide in a reflux apparatus, pydroxaringenin yields phloroglucol and *p*-hydroxy-coumaric acid. Phloretin obtained by the hydrogenation of naringenin failed to cause glycosuria when 1.5 grain was given to a dog (10 kilos). The active results obtained with commercial phloretin are due to the presence of phlorhizin which was found in amounts up to 30%.

N. H. J. M.

Catalytic Decomposition of Borneol in the Presence of Metals and of Metallic Oxides. J. ATOY and V. BRUSTECK (*J. Pharm. Chim.*, 1914, [vii], 10, 49–51).—Borneol is converted into camphor and hydrogen when it is slowly passed over hot, finely divided copper. The yield of camphor increases regularly from 240° to 300°, and is quantitative at the latter temperature if the vapours travel sufficiently slowly over the copper. Above 300° the proportion of camphor decreases; at 350° it is still considerable, but above 400° new liquids are formed resembling the terpenes. With reduced copper, camphor is obtained at 350°, whilst at 450° liquid terpenes are reduced. Iron gives less satisfactory results.

The behaviour of borneol in the presence of the oxides of aluminium, zirconium, uranium, and thorium has also been studied; the latter gives best yields. The experiments are performed in the same manner with the metals; the most favourable temperature is 350° and must exceed 400°. The product is a pale yellow liquid, b. p. 150–180°, σ_0^{20} 0.8637, π^{20} 1.472, $a_1 + 1.46^\circ$. On fractionation it yields pinene, π^{20} 156–160°, D^{20} 0.871, π^{20} 1.472, and a smaller portion, b. p. 130–180°, the nature of which could not be definitely proved.

Terpenes are also formed by the decomposition of borneol in the presence of copper at about 400°, and the product can be separated into bicyclic terpenes, b. p. 155–160°, D^{20} 0.860, and monocyclic diacarbons, b. p. 170–175°, D^{20} 0.850.

H. W.

Action of Ammonium Hydrogen Sulphide on Thujone and Carone. C. AGOSTINELLI (*Gazzetta*, 1914, **44**, ii, 111–115).—Thujone is heated in alcoholic solution with ammonium hydrogen sulphide, which is transformed into isothujone, this then reacting further with sulphide to form a mixture of polysulphides; among the products of decomposition of the latter, only thiothujone could be detected. Under similar treatment, carone yields no isomeride, although its transformation into carvenone, which is effected readily by the action of concentrated sulphuric acid, would be expected. The products obtained were sulphides of the compositions $(C_{10}H_{17})_2S$ and CH_3S_2 .

T. H. P.

Essential Oil of Artemisia arborescens. L. T. JOSA (*Anales Aplicata*, 1914, **2**, 63–68).—Distillation of 2 quintals of the seed-shoots of *Artemisia arborescens* yielded 1140 grams of a dark blue, somewhat viscous, aromatic oil, D^{20} 0.9458, saponification number 29.3, ester number 9.8, ester number 19.5, ester number after acetylation

50·0; it remains clear at -15°. The oil contains: (1) 13·1% alcohols of the formula $C_{19}H_{38}O$, consisting of thujol and a smaller portion of another alcohol, which is apparently borneol; 8·5%; (2) alcohols are in the free state and the remaining 5·36% in the form of esters of fatty acids. (2) Formic, acetic, isovaleric, propionic, palmitic and stearic acids, partially esterified by the above alcohols. (3) About 13% of β -tanacetone. (4) Various hydrocarbons of low boiling point.

T. H. F.

Oils of the Coniferae. I. The Leaf and the Twig Oils of Cuban and Longleaf Pines and the Cone Oil of Longleaf Pine. A. W. SCHÖRGER (*J. Ind. Eng. Chem.*, 1914, **6**, 723-742). The percentage compositions of the oils were found to be, as follows:

	Cuban.		Longleaf.	
	Leaf and twig.	Leaf and twig.	Leaf.	Twig.
Furfuraldehyde	trace	trace	trace	trace
<i>L</i> -Pinene	4	8-9	2	1
<i>L</i> -Camphene	10	13-14	12-13	1
<i>L</i> , <i>B</i> -Pinene	35-36	44	50	1
Dipentene	8	5	5	1
Bornyl ester (as acetate)	3·5	2·4	2	1
Free alcohol (as <i>L</i> borneol)	11·4	10·0	9·8	1
<i>d</i> : <i>l</i> -Pinene	18-19	10-11	11	1
Loss, etc.	9	6	7·5	1

* *d*-*l*-Pinene.

W. P. S.

Components of Essential Oil of Santolina *chamaecyparissus*. L. FRANCESCONI and N. GRANATA (*Gazzetta*, 1911, 44, 150-162. Compare A., 1911, i, 1001; 1912, i, 38).—This essential oil contains two isomeric unsaturated ketones, termed α - and β -santolinones. The α -compound is optically inactive and probably racemic, since its molecule contains an asymmetric carbon atom as its hydroxylamino-oxime can be separated by means of phosphorus pentosulfide into the two antipodal forms. The β -ketone is also inactive and probably racemic. The oil contains further levorotatory γ -ketone, yielding a dextrorotatory oxime. These three ketones do not combine readily with sodium hydrogen sulphite or with free hydrazine and do not yield crystalline products with propylhydrazine, bromophenylhydrazine or bromine. With hydrazine the α -compound gives first the oxime and then the hydroxylamine, but no simple hydroxylamine; the β ketone yields no hydroxylamine oxime, but liquid oxime or the hydroxylamine, one or the other predominating according to the conditions; the γ -compound gives only oxime, and appears to be saturated and of the camphor type. The separation of the three ketones is described.

Like most oximes of saturated and unsaturated ketones, the α - and β -santolinones yield the corresponding ketones when heated with acids, which do not effect isomerisation of these ketones. Consequently the double linking cannot be so placed that it may readily, its α : β -position being thus confirmed. The case

camphoroxime is not easily converted into the ketone by the action of acid and thus resembles camphoroxime.
γ-Anti-isobenzoquinoneimine, $C_{10}H_{17}ON$, forms large, rounded prisms, m. p. 16–17°, $[\alpha]_D + 41^\circ$. Its hydrochloride forms long prisms, m. p. 43–45°, $[\alpha]_D + 64.31^\circ$.

T. H. P.

Mesobilirubin. HANS FISCHER (*Ber.*, 1914, **47**, 2330–2333).—It is recently stated (this vol., i, 888) that bilirubin, like haemin, may be reduced to a substance which yields methylethylmaleimide on subsequent oxidation. This substance, mesobilirubin, is now described. When shaken with sodium amalgam, it is further reduced to hemi-bilirubin, and, on the other hand, it is formed when hemibilirubin is acted with potassium methoxide. The by-product II, which is formed during the reduction of the bile pigment to hemibilirubin, also yields mesobilirubin under the latter conditions. There is, therefore, the misconception between these compounds that there is between haemin, haemoporphyrin and porphyrinogen, and it is suggested that the name "mesobilirubin," which gives a wrong idea of the relative weight of the molecule, should give place to *mesobilirubinogen*.

For the preparation of *mesobilirubin*, $C_{32}H_{38}O_4N_4$ or $C_{32}H_{38}O_6N_2$, bilirubin was dissolved in 0.1*N*-sodium hydroxide and shaken with basal palladium in presence of hydrogen, using three portions of or of a 1% solution of the preparation for 5 grams of the pigment. The new pigment was then precipitated by acetic acid and obtained in light-yellow, slender, felted needles or stout prisms, m. p. 315° (brom.) which responded to Gmelin's reaction, but not to Ehrlich's iodoform test.

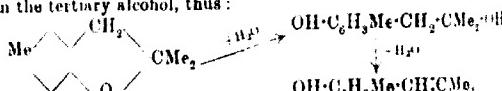
During the distillation of a mixture of the esters of bilirubin and *β*-ketopyrrolicarboxylic acids (this vol., i, 430) a deep yellow compound separated, which is now identified as an oxidation product, namely, *methyl xanthobilirubate*, $C_{16}H_{24}O_8N_2$. It forms slender prisms, m. p. 212°.

J. C. W.

The Pigments of Fusarium. BEZSONOFF (*Compt. rend.*, 1914, **59**, 448–450).—Using the method of Willstätter and Mieg (see part A., 1907, i, 865) the author has isolated two pigments from the colouring matter of *Fusarium orobanchus*, one a yellow anthocyanin pigment, soluble in water and alcohol, the other a red carotene. The latter is identical with that described by Willstätter and Mieg, with respect to its behaviour towards solvents, being, however, more soluble in chloroform than in carbon disulphide. It crystallises in plates. It loses colour in solution under certain conditions, a violet modification being obtained in alcoholic solution, reddish-violet in solution in benzene, and yellow after boiling in cymene. The three modifications show a broad absorption band at the left of the spectrum and two new bands between this and the middle of the spectrum, all the bands showing gradual displacement in passing from the violet to the yellow modification. The yellow anthocyanin pigment crystallises on evaporating its aqueous solution, and is always accompanied by sugar, behaves as a weak acid and readily combines with bases.

W. G.

1 : 1 : 4-Trimethylcoumaranone. K. von Auwers (*Ber.*, 1911, **47**, 2334—2350).—In continuation of a study of 1-alkylcoumarans (compare A., 1912, i, 1009) attempts have been made to prepare 1 : 1-dialkyl derivative. In view of the mobility usually displayed by a halogen atom when attached to a tertiary carbon atom, it was expected that *m*-bromo-isobutyryl-*p*-cresol, $\text{OH}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CMe}_2\text{Br}$, would even more readily suffer condensation to a coumaranone than the *a*-halogenated *o*-acetyl- or *o*-propionyl-phenola. Indeed, it did seem to be improbable that the coumaranone would be formed directly during the preparation of the butyryl derivative by the condensation of *a*-bromo-isobutyryl bromide with *p*-tolyl methyl ether. However the sole product of this Friedel-Craft's synthesis is the above *m*-bromo-isobutyryl-*p*-cresol (80% yield), which is all the more remarkable since, under the influence of aluminium chloride, the bromine might least have been replaced by chlorine. When treated with zinc dust and acetic acid, the compound simply yielded *m*-isobutyryl-*p*-cresol (future communication), whilst, under the influence of alkaline agents it merely exchanged bromine for hydroxyl, to form the tertiary alcohol $\text{OH}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CMe}_2\text{OH}$. Strange to say, this compound was quite stable towards such dehydrating agents as formic acid, phosphorus trichloride, 30% sulphuric acid, alcoholic hydrogen chloride or potassium hydrogen sulphate. Since the desired condensation could not be effected by the above schemes, the action of organic bases on the *a*-bromo-isobutyryl-*p*-cresol was tried. It was found that dimethyl- and diethyl-anilines bring about the desired end, whereas pyridine, in an unaccountable manner, yields *p*-hydroxytoluic acid. The most characteristic derivative of the new 1 : 1 : 4-trimethylcoumaran is the semicarbazone. It was expected that this compound would yield 1 : 1 : 4-trimethylcoumaran when heated with sodium ethoxide, what seemed, at first, to be the case, for an apparently indifferent oil of the right percentage composition was obtained. Later, this was recognised, however, as a weak phenol, namely, 2-hydroxy-5-*o*-methylstyrene (compare *o*-hydroxy-*aa*-diphenylethylene, Stoemer and Kippe, A., 1904, i, 182), formed by the addition of water to the coumaran, with opening of the ring, followed by elimination of water from the tertiary alcohol, thus:



This phenol was also synthesised by the action of magnesium *o*-bromide on *p*-homosalicylaldehyde. Most of its derivatives must be oils, but it yielded the well-defined 4-*o*-trimethylstyroxyacetophenone when warmed with chloroacetic acid.

The above compounds form material for spectro-chemical investigations which will be described later.

***m*-a-Bromo-isobutyryl-*p*-cresol.** $\text{OH}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CMe}_2\text{Br}$, is a yellow oil, b. p. 154°/12 mm., 156—157°/13 mm., 166—167°/22 mm. D_4^{20} 1.3669, D_4^{∞} 1.370, n_a 1.56400, n_b 1.57141, n_p 1.59245, n_d 1.59250 at 22.3°, n_b^2 1.5724, and its acetals has b. p. 182—183°/17 mm. D_4^{20} 1.3173, D_4^{∞} 1.324, n_a 1.52435, n_b 1.52883, n_p 1.54054, at 27

* 15314. The cresol gradually dissolves in dilute aqueous sodium hydroxide, yielding *m*-*a*-hydroxyisobutyryl-*p*-cresol, which crystallises from light petroleum in small, flat, yellow, sparkling prisms, m. p. 56–58°. It has b. p. 161–162°/18 mm., D₄²⁰ 1.0243, n_D²⁰ 1.52824, μ_{D}^{20} 1.55370, η_D 1.55342, n_D 1.57053 at 54°, gives a violet coloration with ferric chloride, and is readily oxidised by hydrogen peroxide to ketone and *p*-hydroxytoluic acid. Its *diacetate*, C₁₂H₁₄O₄, forms glistening, rhombic plates and long, flat needles, m. p. 57°, b. p. 182–187°/18 mm., and its *methyl ether*, OMe-C₆H₄Me-CO-CMe₂-OH, prepared by means of methyl sulphate or sodium and methyl iodide, separates from light petroleum in long, flat, lustrous prisms, m. p. 51–51.5°, b. p. 50–164°/24 mm. The *semicarbazone*, C₁₂H₁₂N₂O₃, is quickly formed at 30–40°, and crystallises in slender needles, m. p. 227–228° (decomp.). The *semicarbazones* of the methyl ether, C₁₃H₁₄N₂O₃, may be prepared from the foregoing semicarbazone, but more readily from the methyl ether, in slender, white needles, m. p. 188–189°.

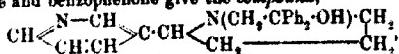
1,1,4,7-timethylcoumaranone, $C_6H_3Me<sup>CO</sub>₍)CMe₂, is best prepared by boiling the above *m*-*a*-bromoacetylbutyl *p*-cresol with diethylamine, pouring the solution into cold, dilute sulphuric acid, converting the distilled oil into the semicarbazone, decomposing this by means of concentrated oxalic acid solution and redistilling. It forms colourless, porous prisms, m. p. 34°–35°, b. p. 137°–140°/10 mm., 145°/18 mm. The physical constants for two specimens are given, the more trustworthy being b. p. 159.5°–161.5°/26 mm., D_{25}^{20} 1.1144, D_{15}^{15} 1.115, n_{D}^{20} 1.54876,
 n_{D}^{20} 1.55475, n_d 1.57109, n_f 1.58711, at 20.6°, n_D^{20} 1.55550. It is quickly oxidized by hot hydrogen peroxide to *p*-homosalicylic acid. Its semicarbazone forms small, white, glistening needles, m. p. 232°, and its m.e. has m. p. 128°–129°, and sublimes on the water-bath. When the semicarbazone is heated with sodium and alcohol at 160°–170° for one hour, it is converted into 6-hydroxy-3-methylstyrene, which separates when the solvent is removed and the residue is diluted with ether, as a pleasant smelling, colourless oil, b. p. 114°–117°. A purer specimen, b. p. 121°–121.4°/13 mm., was obtained by the interaction of magnesium isopropyl bromide and *p*-homosaliclylaldehyde. The stony carbinol which is first formed gradually suffers the necessary loss of water on distillation under 20 mm. pressure, but it is best not attempt to expedite this by using dehydrating agents. The compound is a phenol for it dissolves in concentrated sodium hydroxide, forms a methyl ether, $C_{12}H_{16}O$, b. p. 117.2°–117.6°/11 mm., and reacts with chloroceric acid in alkaline solution, yielding 4-methyl-2-isopropenylphenoxycetic acid, $(CO_2H-CH_2-O-C_6H_3Me-CH=CH)CMe_2$, in silky, fine needles, m. p. 80°–81°.$

J. C. W.

Organic Syntheses by Means of Sunlight. X. Behaviour of Vegetable Alkaloids towards Ketones. E. PATERNO [with C. CAVAZI and R. DE FAZI] (*Gazzetta*, 1914, 44, ii, 99-111. Continue this vol., ii, 321).—The following pairs of compounds have been exposed to the action of light for some months and the resulting mixtures investigated.

Coniine and benzophenone yield benzopinacone, indicating that the alkaloid loses hydrogen.

Nicotine and benzophenone give the compound,



crystallising in needles, m. p. 151—153°.

Sparteine and acetophenone yield acetophenonepinacone and a gelatinous base, the *platinichloride* of which has the composition $\text{C}_{15}\text{H}_{20}\text{N}_2\text{C}_6\text{H}_5\text{O}_2\text{H}_2\text{PtCl}_6$ (1); the base exhibits colloidal properties and shows shining, red granules of ultramicroscopic dimensions.

Sparteine and benzophenone give benzopinacone and a yellow compound which is apparently an additive compound.

Piperine and benzophenone yield benzopinacone, a white compound, m. p. 158—165°, and a small proportion of a yellow compound, m. p. about 200°.

Papaverine and acetone remain without apparent change.

Strychnine and acetophenone yield an amorphous, yellow compound turning brown but not melting at 280°, and forming a *picrate* which corresponds with that of a compound of 1 mol. of strychnine and 2 mol. of the ketone. On prolonged exposure to air at 100° the compound loses about 10% of its weight, and when left under a jar in presence of acetophenone, absorbs the latter in large proportion as much as 76% being taken up in about three and a-half hours. The compound has marked emulsifying properties.

Strychnine and benzophenone seem to yield a polymeride of strychnine capable of absorbing large proportions of the ketone. The resulting product is a yellow, amorphous substance which does not melt at 300°.

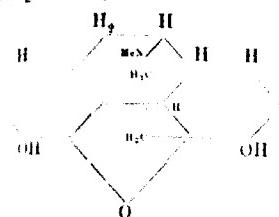
Narcine and acetone give: (1) A base which forms shining lamellae, m. p. 231—232°, and is apparently a dehydrated narcine of the formula $\text{C}_{22}\text{H}_{22}\text{O}_7\text{N}$; its *platinichloride* and *picrate*, m. p. 156—157°, were analysed; cryoscopic measurements in acetic acid gave inconclusive results; (2) a base, $\text{C}_{22}\text{H}_{22}\text{O}_7\text{N}$ (1), which crystallises in plates, m. p. 156—160°, and forms a *hydrochloride*, m. p. 196—197°, and a *sulfate chloride*.

Narcine and acetophenone yield an intensely reddish-brown, amorphous powder, beginning to decompose at about 220°.

Narcine and benzophenone give a reddish-brown crystalline compound which is being examined further. T. H. F.

Investigations of the Morphine Alkaloids. I. J. von Dittmer [with O. KRÜBER and E. AUST] (*Ber.*, 1914, **47**, 2312—2331). According to the formulæ usually assigned to morphine and the like (compare KAORR and HÜRLEIN, *A.*, 1907, i, 789) there is, in each case, double linking in the β -position with regard to the nitrogen atom. The author has shown, in a number of papers (compare *A.*, 1913, 189) that cyanogen bromide readily ruptures such a chain at the nitrogen atom, rather than remove a methyl group from the ring. Applying this reaction to acetylated α -methylmorphimethane and its salts, dark oils are formed if the hydroxyl groups in these alkaloids are esterified.

protected), which has no double linking in the $\beta\gamma$ -position, it is found that the compound behaves like trimethylamine or dimethylaniline, the basic group, NMe_2 , being converted into the non-basic group NMe^+CN . This shows that the complicated structure of the other parts of the molecule does not interfere with the specific action of the cyanogen bromide. Thebaine, however, does not lose the N -methyl group, but seems to combine directly with the reagent. Morphine and codeine, on the other hand, in the form of their acetyl derivatives, do not suffer rupture of the ring, but exchange a N -methyl group for nitrogen. Dihydromorphine, dihydrocodeine, and, probably, tetrahydrothebaine (Oldenborg, A., 1913, i, 1093) behave in the same way. The author therefore draws the conclusion that the particular double linking in morphine and codeine is not in the $\beta\gamma$ -position, that is



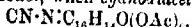
either 8:14 or 13:14, and suggests that, in contrast to thebaine, there is no double linking, but rather a bridge between the atoms 6 and 8. The annexed formula is therefore proposed for morphine. This would help to explain many of the problems connected with the constitution of morphine;

among others, the facts that it is very difficult to eliminate hydrogen chloride from chloromorphide and to combine bromine with the碱.

The cyano-acetyl derivatives, obtained from morphine and codeine, have also been hydrolysed, first to the acetyl-free compounds, and finally to normorphine and norcodeine. The discovery of the latter substance (N -demethylcodeine) by Diels and Fischer (this vol., i, 989) caused the author to give the present early account of what was intended to be an exhaustive study of these compounds.

Cyanogen bromide (1 mol.) is added to a concentrated chloroform solution of acetyl-methylmorphinethine (1 mol.) and warmed for two hours. On diluting the solution with ether, the methobromide of the base separates together with some of the non-basic cyano derivative, $\text{C}_{12}\text{H}_{18}\text{O}_2\text{N}_2$. The latter is present in the filtrate, and crystallises from ether in silvery leaflets, m. p. 108°. The residue, insoluble in ether, almost completely soluble in hot water, from which the acetyl-methylmorphinethine methobromide, $\text{C}_{12}\text{H}_{18}\text{O}_2\text{NBr}$, separates, on cooling, in large scales, m. p. 207—208°. The acetyl-cyano-derivative dissolves easily in a solution of sodium methoxide, and, on adding water immediately, the non-acetylated cyano-derivative, $\text{C}_{12}\text{H}_{18}\text{O}_2\text{N}_2$, separates, to form an ice-flower-like mass of crystals, m. p. 119°.

Diacetylmorphine (heroin) also reacts with cyanogen bromide under similar conditions. On diluting with ether, the whole of the product separates. Part is soluble in cold alcohol and consists of heroin methobromide, which could not be purified. The residue may be crystallised from hot alcohol, when *cyanodiacetylnormorphine*,



separates as a crystalline powder, m. p. 240°, the yield being 75 grams from 100 grams of diacetylmorphine and 40 grams of cyanogen bromide. *Diacetyldihydromorphine*, $C_{21}H_{22}O_5N$, prepared from the product of the catalytic reduction of morphine, m. p. 167°, forms *cyanodiacyldihydromorphine*, $C_{21}H_{22}O_4N_2$, in long, silky needles, m. p. 138—139°. The chloroform solution of the product in the case of acetylcodeine is best evaporated to dryness and freed from methobromide by boiling water. *Cyanoacetylnorcodeine*, $CN\cdot NC_{16}H_{14}O(OMe)\cdot OAc$,

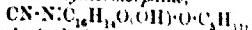
forms minute crystals, m. p. 184°. *Acetyl dihydronorcodeine*, $C_9H_{18}O_3$, m. p. 129°, yields *cyanooacetyl dihydronorcodeine*, $C_{20}H_{22}O_4N_2$, in glaucous crystals, m. p. 227—228°.

In order to remove the acetyl groups from cyanodiacyl normorphine it is best to dissolve the substance in a solution of potassium hydroxide (2 mol.) in 5% alcohol at 50°, and, after five minutes, not longer, to dilute with cold water and acidify with acetic acid. *Cyanomorphine*, $CN\cdot NC_{16}H_{14}O(OH)_2$, separates as a fine powder, $\pi = 295$ —296°, which is not indefinitely stable in alkaline solution, but can be directly acetylated to the mother substance, and, like morphine, it yields a monobenzoyl derivative, $C_{24}H_{20}O_4N_2$, m. p. 265°, which is insoluble in alkalis. The analogous hydrolysis of cyanocodeine or codeine is best effected by dissolving the substance in warm concentrated hydrochloric acid and diluting after five minutes. *Cyanonorcodeine*, $CN\cdot NC_{16}H_{14}O(OMe)\cdot OH$, m. p. 263°, is also easily prepared by the methylation of cyanonormorphine.

The further hydrolysis of these cyano-derivatives presents no difficulties, but may be accomplished by warming the compound in 6% hydrochloric acid for several hours, when the salts of the base crystallise on cooling. Starting with codeine, it is possible to obtain a 38% yield of pure norcodeine in a few days, whereas De la Fosse's Fischer's method gives a 16% yield. Norcodeine (*N*-demethyl codeine), $NH\cdot C_{16}H_{14}O(OMe)\cdot OH$, crystallises in leaflets, m. p. 224°. The sulphate, nitrate, and acetate are readily soluble, the sparingly soluble *hydrochloride*, m. p. 309°, crystallises with $3H_2O$, the *chloride* forms yellow leaflets, m. p. 239°, and the *hydriodide*, m. p. 257°, combines with $2H_2O$. Acetic anhydride gives rise to a benzyl derivative, but phenylthiocarbimide attacks only the imino group forming a *phenylthiocarbamyl* derivative, $C_{17}H_{15}O_3N\cdot CS\cdot NH_2$, m. p. 210°, whilst the addition of sodium nitrite to an acid solution precipitates the *nitroso*-derivative, $C_{17}H_{15}O_3N_2$, which crystallises as yellow leaflets, m. p. 246°. *Normorphine*, $NH\cdot C_{16}H_{14}O(OH)_2$, m. p. 262—263°, could not be obtained quite pure, for it is appreciably soluble only in hot water or alcohol, and decomposes under treatment. It is unstable towards alkalis, but yields a number of well-defined derivatives. The *hydrochloride*, $1H_2O$, has m. p. 266°; the *platinichloride*, $3H_2O$, m. p. 230—231°; the *sulphate*, $3H_2O$, is less soluble, the *triacetyl* derivative forms tablets, m. p. 164°; the *hydrochloride* forms white leaflets, m. p. 208°, and the *phenylthiocarbamyl* derivative is a colourless powder, m. p. 245°. The assumption that the oxide ring remains intact through all these changes is justified by the conversion of normorphine and norcodeine, by direct methyl-

as codeine methiodide and then, by the action of alkali, into α -methylmorphethine.

Cyanonormorphine reacts with isoamyl iodide in presence of sodium iodide to form *cyanisoamylnormorphine*,



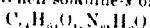
$m.p. 225^\circ$, which may be hydrolysed as above to *O isoamylnormorphine*, $\text{HC}_6\text{H}_{11}\text{O(OH)-O-C}_2\text{H}_{11}$, $m.p. 106^\circ$; this forms a sparingly soluble *chloride*, $m.p. 278^\circ$, and a *nitroso*-derivative, $m.p. 186^\circ$.

The silylation of the imino group of norcodeine is easy. Thus, on using the compound with β -phenylethyl iodide in chloroform, *phenylethylnorcodeine*, $\text{CH}_2\text{Ph-CH}_2\text{N(C}_{14}\text{H}_{11}\text{O(OMe))OH}$, is obtained. This is isolated by adding sodium carbonate solution, extracting in chloroform, dissolving the residue from the evaporated extract in acetic acid, and adding sodium nitrite; when a solution of the nitro of the tertiary base and a precipitate of nitrosonorcodeine is obtained. The latter is extracted with hot water, and the concentrated solutions of the nitro are rendered alkaline. The new base $m.p. 114^\circ$, the *hydrochloride*, $m.p. 277^\circ$, is sparingly soluble, and its *platinichloride* has $m.p. 216-217^\circ$.

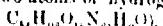
The experiments with thebaine and tetrahydrothebaine were somewhat indefinite.

J. C. W.

Solanum Sodomaeum. VI. GIUSEPPE ODDO and MARCELLO CENARIS (*Gazzetta*, 1914, **44**, i, 680-690. Compare A., 1911, i, 670; *ibid.* A., 1911, i, 671).—When solanine-s of the formula



boiled with dextrose for a long time and then recrystallised, it is said to have taken up two atoms of hydrogen (formula



though its physical and chemical properties are unchanged. The gain of the dextrose is not a reduction, but a separation of impurities which contain less hydrogen. When solanine-s which has been boiled as far as possible with water and alcohol is boiled with ether and benzene, a small quantity of a saturated *hydrocarbon*, $\text{C}_{18}\text{H}_{36}$, which forms colourless, silky needles, $m.p. 58-60^\circ$, is obtained. In another experiment the hydrocarbon was accompanied by a white, iridescent substance, $m.p.$ about 300° . The solanine-s recovered after this treatment and purified with water and alcohol has the composition $\text{C}_{24}\text{H}_{36}\text{O}_{18}\text{N}_2\text{H}_4\text{O}$. Solanine-s may crystallise with one or two molecules of water. Solanine-s absorbs traces of carbon dioxide when kept in contact with air.

R. V. S.

Solanine-s. VII. Identification of the Second Hexose formed on Hydrolysis. GIUSEPPE ODDO and MARCELLO CENARIS (*Gazzetta*, 1914, **44**, i, 690-696. Compare preceding abstract). The authors have definitely identified the second hexose formed on hydrolysis of solanine-s and find that it is dextrose.

R. V. S.

Sphingosine. III. The Oxidation of Sphingosine and Hydroosphingosine. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, **18**, 481-484. Compare A., 1912, i, 284, 575; this vol., i,

308).—The authors show that the tridecoic and pentadecic acids obtained by the oxidation of sphingosine and dibydroosphingosine respectively, and their amides, are identical with the corresponding normal acids and amides prepared synthetically (see this vol., i, 111). The carbon atoms in the sphingosine molecule are therefore arranged in a normal chain. The cleavage products of the ozonide of sphingosine are tridecoic acid and a substance which gives some of the reactions of an amino-tetrose. H. W. K.

Pyrrole Group. XI. Action of Tertiary Pyrroles on Organic magnesium Compounds. BERNARDO ODDO (*Gazzetta*, 1914, **44**, 706—713).—The author has repeated some of the work of Hess and Wissing (this vol., i, 725) and finds that pure methylpyrrole has no action on magnesium ethyl bromide. When acetyl chloride is added to the mixture, 2-acetyl-1-methylpyrrole is produced, but the substance is also formed in these circumstances by the direct action of acetyl chloride on the pyrrole alone. Similar results are also obtained with 1-benzylpyrrole. The contradictory observations of Hess and Wissing are to be ascribed to the presence of free pyrrole in the 1-methylpyrrole used by them. R. V. S.

Pyrrole Group. XII. Alkylation of Pyrroles. II. ELENA Oppo and ROMALDO MANELLI (*Gazzetta*, 1914, **44**, ii, 162—174).—The formation of 2- and 3-methylpyrroles by the action of methyl iodide on magnesium pyrrol bromide (this vol., i, 80) is confirmed by the conversion into pyrrole-2- and pyrrole-3-carboxylic acids by fusion with potassium hydroxide, and that of 3-methylpyrrole also by the formation of the corresponding acetyl-cinnamoyl derivatives. Further confirmation of the structures of these methylated pyrroles has been obtained by their reactions with hydroxyamine (compare Ciamiciani and Zucchi A., 1891, 1502), which yields principally β -methylsuccinidoxime together with a small proportion of levuidaldoxime.

Application of these reactions to the products of the interaction of ethyl iodide and magnesium pyrrol bromide shows that these products consist of 3-ethylpyrrole, 2:5-diethylpyrrole and, if the reaction takes place in absence of solvent, also 2:3:4- or 2:3:5-triethylpyrrole, $C_{10}H_{17}N$, which is a pale yellow liquid, b. p. 200—205°.

Similarly, the action of propyl iodide on magnesium pyrrol bromide yields: (1) 3-propylpyrrole (b. $C_7H_{11}N$, b. p. 176—179°/75 mm., which is perhaps identical with that obtained by Zucchi (A., 1891, 1502); (2) a dipropylpyrrole, $C_{10}H_{15}N$, b. p. 123—126°/15 mm., and (3) 2:3:4- or 2:3:5-tripropylpyrrole, $C_{13}H_{23}N$, b. p. 207—210°/15 mm., 150—160°/15 mm. T. H. F.

Indigotin. V. Halogenated Indigotins and Derivatives. E. GRASIMOLGIN and P. SKYDER (*Ber.*, 1914, **47**, 2365—2373; *Chemist* A., 1910, **74**, 339).—An account is given of several halogenated indigotins, many of which are technical products, and of the isatins which they yield on oxidation. The positions of the absorption bands and solubilities are the factors which receive most notice.

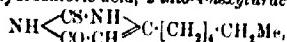
5:7:5':7-Tetrachloroindigotin (brilliant indigo B) was oxidized to

β -dichloroindatin, and this converted into the β -phenylhydrazone, $C_8H_7O_2NCl_2$, brilliant saffron-yellow crystals, m. p. 296—297°, and the β -oxime, $C_8H_7O_2N_2$, canary yellow crystals, decomp. 255°. $4:4'$ -Bromo- $5:5'$ -dibromoindigotin (brilliant indigo 4G), yielded 4-chloro-indazolinatin, $C_8H_7O_2NClBr$, m. p. 273—274°, which sublimes with ease in vapours and forms a phenylhydrazone, ochre-yellow crystals, m. p. 278°, and an oxime, m. p. 253—254° (decomp.). The constitution of the indatin was established by conversion into 3-chloro-4-bromo-aniline on distillation with potassium hydroxide. $4:7:4:7$ -Tetra-chloroindigotin was converted into $4:7$ -dichloroindatin, $C_8H_7O_2NCl_2$, brilliant orange-yellow crystals, m. p. 252°, and this into the phenyl-hydrazone, m. p. 265°, and oxime, m. p. 245° (decomp.). $3:6:7$ -Tetrachloroindatin (Orndorff and Nichols, A., 1913, i, 93) yielded $3:6:7$ -dichloroindatin, $C_8H_7O_2NCl_2$, an ochre yellow substance, m. p. 24—295°, which was converted into tetrachloroaniline, and into a methylhydrazone, m. p. 293°. $6:6'$ -Dibromoindigotin and $6:6'$ -di-aminoindigotin were prepared from $6:6'$ -diaminoindigotin through a benzozonium sulphate. They crystallise from methyl benzoate, the latter in dark, bluish-violet crystals. $6:6'$ -Diaminoindigotin is valuable as a dye, but, on bromination, it yields a brown dye (brown R) (D.R.P., 221531), which, as is now shown, consists really of $5:7:5':7'$ -tetrabromo- $6:6'$ -diaminoindigotin, for, on treating the amino-groups by diazotisation, it was converted into the $5:7:5':7'$ -tetrabromoindigotin, which was degraded to $5:7$ -aminoindatin (β -phenylhydrazone, m. p. 297—298°, β -oxime, decomp. 221°, and finally to $2:4$ -dibromoaniline.

J. C. W.

Pyrimidines. LXXII. Synthesis of 4-Hexyluracil and its relationship to Uracil-glucosido. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1914, **36**, 1891—1899).—In earlier papers (Johnson and Bernoff, A., 1913, i, 656; this vol., i, 1031), the synthesis and properties of the simplest nucleosides of thymine and uracil have been treated. The constitution of these compounds was established by reduction with hydriodic acid to $4:5$ -dimethyluracil and methyluracil respectively. As the higher homologues of these nucleosides ought theoretically to be capable of a similar interaction with hydriodic acid, it is desirable that the higher homologues of methyluracil and the corresponding thymine compounds should be re-visited. An account is now given of the synthesis of 4-hexyluracil, which may be regarded as the reduction-product of uracil-nucleoside.

When ethyl heptoacetate (Wahl and Doll, A., 1913, i, 532) is used with thiocarbamide in an alcoholic solution of sodium borohydride, condensation takes place with formation of the sodium salt of 2-thio-4-hexyluracil. On acidifying an aqueous solution of the sodium salt with hydrochloric acid, 2-thio-4-hexyluracil,



m. p. 145°, is obtained, which crystallises in colourless needles. By heating this compound with an aqueous solution of chloroacetic

acid, it is converted quantitatively into 4-hydroxysuccil (4-hydroxy-
hydropyrimid.2:6-dione), $\text{NH} < \text{CO} \cdot \text{NH} > \text{C} \cdot [\text{CH}_2]_4 \cdot \text{CH}_2\text{Me}$, m. p. 110°,
which forms lustrous plates. E. G.

Allantoin. Maurice H. Givens (*J. Biol. Chem.*, 1914, **44**, 417—424). Allantoin in aqueous solution undergoes slow decomposition. In distilled water the loss was found to be 6.3% in 629 days in tap water, 6.4% in 24 days. The product gives off ammonia on distillation with magnesium oxide. Allantoin is also quickly destroyed by alkali and by fecal bacteria. It disappears rapidly in a kidney urine, but is apparently stable if the urine is made acid.

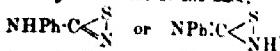
In the estimation of allantoin in a series of samples by Wiechowicz's method, the analyses must be carried out as quickly as possible to the point of precipitation of the allantoin by the mercuric acetate—soda acetate reagent. They can then be set aside, if desired, as this compound is quite stable even in the presence of excess of the xanthine reagent. H. W. P.

Electrical Conductivity of Tetrazole and its Derivatives at Various Temperatures. E. OLIVERI-MANDALÀ (*Gazzetta*, 1914, **44**, ii, 175—180).—The author has measured the conductivity of tetraza-tetrazolamide, and bi-tetrazole at various temperatures. With mean temperature, the temperature coefficient of the conductivity diminishes with bi-tetrazole, but increases with tetrazole and the amide. The value of the dissociation constant increases regularly with rise of temperature, the value at 35° being almost double (or treble) that at 0° in the case of tetrazole (or the amide). This increasing ionisation of tetrazole and its amide is interpreted on the basis of its tautomerism exhibited by the nucleus (compare A., 1913, i, 132), a equilibrated mixture of the two forms probably existing in solution. T. H. P.

Constitution of Phenylsulphotetrazoline and of Thio-sulphol. E. OLIVERI-MANDALÀ (*Gazzetta*, 1914, **44**, i, 670—671).—Investigating the product described as thiophenyltetrazoline and triazosulphol by Freund and Hempel (A., 1895, i, 193) and Freudenthal and Schwarz (1897, i, 125), the author finds that the chemical behaviour of the substances obtained by Freund by the action of nitrous acid on fatty derivatives of thiosemicarbazide is identical with that of the substances from aromatic derivatives, the difference being only one of stability. Azimide acts on the esters of methylisothiocarbimide and ethylthiocarbimide, yielding the same substance as Freund obtained from the corresponding thiosemicarbazides, and from aromatic thiocarbimidies (*o*- and *p*-tolyl) similar compounds are formed. The chemical behaviour of all these substances shows them to be thiocarbamoylazomides of the type $\text{R} \cdot \text{NH} \cdot \text{CS} \cdot \text{N}_\text{H}$, and by this formula all their reactions and decompositions may be explained.

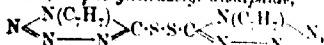
When phenylthiocarbamoylazomide is boiled with concentrated hydrochloric acid, a substance crystallising in needles, m. p. 240°—250°,

obtained. It is the hydrochloride of the base,



The base forms lustrous leaflets, m. p. 121–123°.

p-Tolylthiocarbamoylazosinimide, $\text{C}_6\text{H}_5\text{NH-C}\equiv\text{S-N}_2$, crystallises in needles, m. p. 140–144°. When it is treated with alkali carbonates, an isomeride, 5-thiol-1-p-tolyltetrazole, $\text{N} \begin{cases} \text{N-C}_6\text{H}_5 \\ \text{C-SH} \end{cases} \text{N}_2$, is formed; it crystallises in needles, m. p. 150–151°. The sodium salt has the formula $\text{C}_6\text{H}_5\text{NH}_2\text{SNa}$. When the mercaptan is oxidised with an alcoholic solution of ferric chloride, di-p-tolyltetrazole disulphide,



is obtained. When the oxidation is effected with alkaline permanganate in the cold, potassium *p*-tolyltetrazolesulphonate is formed, together with probably the potassium salt of hydroxytolyltetrazole.

By oxidation of the mercaptan with alkaline permanganate in the warm, hydroxytetrazole-1-benzoic acid, $\text{N} \begin{cases} \text{N-C}_6\text{H}_5\text{CO}_2\text{H} \\ \text{N-C-OH} \end{cases}$, can be obtained.

This salt has the formula $\text{C}_8\text{H}_4\text{O}_3\text{N}_2\text{Ag}_2$.

R. V. S.

Apparent Formation of Euglobulin from ψ -Globulin and the Relationship between these two Proteins in Serum. HARRIETTE BAUER (*Biochem. J.*, 1914, 8, 404–420). Solutions of ψ globulin from horse serum when subjected to dialysis deposit large quantities of a water-insoluble protein resembling euglobulin. The author brings forward evidence tending to show that this euglobulin is derived from the ψ globulin by a gradual process of denaturation, which is accompanied by a disappearance from the solution of the small amount of phosphorus originally present in the ψ globulin preparation. When the phosphorus has disappeared from the solution, the precipitation of euglobulin ceases, but the denaturation process can be re-initiated by adding more phosphorus in the form of a watery emulsion of calcium together with a trace of acid or alkali, or a little salt (for example, 1% of sodium chloride) to prevent the precipitation of the ψ globulin.

The euglobulin thus artificially produced appears to be a mechanical complex resulting from the interaction and mutual precipitation of the two colloidal systems: (a) the solution of ψ globulin and (b), the lipid emulsion, and it is suggested that the euglobulin in serum is a protein-gold complex of similar origin. This view is supported by (a) the constant phosphorus content of euglobulin; (b) the readiness with which phosphorus can be removed from euglobulin by extraction with acetone and ether, during which process the property of salt solubility is lost. It can, in some cases, be restored by the addition of the extracted oily substance or of lecithin to the extracted euglobulin; (c) the similarity in chemical composition between ψ -globulin and euglobulin; (d) the want of accurate coincidence between the isoelectric point of ψ -globulin and the point of optimum flocculation, as pointed out by FAIOL (this vol., ii, 547).

H. W. B.

Action of Diazomethane on Caseinogen. ARTHUR GRAF and MAXIMILIAN NIERKETHEIN (*Biochem. J.*, 1914, **8**, 287—292). Compere Krause and Skrup, *A.*, 1909, i, 748, and Herzog and Landsteiner, *ibid.*, vol., i, 753).—Caseinogen on treatment with diazomethane in ether solution undergoes methylation, forming methylcaseinogen, which is a light colourless powder indistinguishable in appearance from caseinogen. It dissolves very slowly in dilute acids and alkalis and gives positive Millon's, Adamkiewicz's and the other protein reactions. Its alkaline solution is optically active. The mean composition of the substance is C 55.31, H 7.32, N (by Kjeldahl) 14.84, N (by Dumas) 15.49, S 0.800, P 0.755 per cent. with 4.36 per cent. of methyl oil, as estimated by the Herzog and Meyer method. Caseinogen has been found to contain 0.88 per cent. of methyl. H. W. R.

A Chemical Compound obtained from Wool and Indigo. M. FORT and L. L. LLOYD (*J. Soc. Dyers.*, 1914, **30**, 297—298). A pure Green, Gardner, Lloyd and Frank, *ibid.*, 1913, **29**, 227). By extracting indigotin wrapped in flannel with boiling acetic acid and diluting the extract with water, a precipitate is formed which is fairly constant in composition and contains the whole of the original indigo together with some of the wool products. This precipitate seems to be a chemical compound. On heating it with dilute sodium hydroxide the wool substance is dissolved and the original weight of indigo is left behind. Further, on boiling the precipitate with pyridine, a precipitating by the addition of 50% alcohol, and boiling the second precipitate with formic acid and reprecipitating with water, the final precipitate was found to have practically the same weight and composition as the original precipitate. Solution in hot naphthalene followed by reprecipitation with alcohol does not affect the composition or weight of the precipitate. This chemical compound is also obtained by extracting indigotin wrapped in flannel with pyridine and adding 50% alcohol to the extract. Its formation helps to explain the greater fastness of indigo tin dyed on wool to that dyed on cotton and silk; in the former case stripping with solvents is more difficult. W. G.

The Variations of Gluten. MARCHADIER and GOUJON (*J. Pure Chim.*, 1914, [vii], **10**, 191—202; compare Collin, *ibid.*, 1898, vi, 97, 150, 200; Balland, *ibid.*, 1899, [vi], **9**, 239, 286, 374 [vii], **9**, 510).—The abnormal diminution in the percentage of coagulable gluten in wheat-flour produced by mixing with flour from buckwheat, barley, rice, maize, etc., is also produced by admixture of inorganic substances such as powdered talc, magnesia or silica. This is not due to a variation in the ratio gliadin to glutelin, but to a variation in the sum of the gliadin and glutelin. Germination, milling, preservation of the flour either in a moist case or in a humid atmosphere, and unfavourable meteorological conditions during the growth of the corn produce a similar diminution in the percentage of coagulable gluten, due in this case to the conversion of gliadin into glutelin or vice versa, thus altering the ratio of these closely allied substances. The authors suggest that the diminution in all these cases is due to a rise in the acidity of the flour under

ditions named, the coagulation of gluten being known to be materially hindered by a very slight rise in the acidity. This rise in acidity has been found in flour after storing and after the addition of rye flour.

W. G.

Sphingomyelin. II. P. A. LEVENE (*J. Biol. Chem.*, 1914, **18**, 43-46; compare **A.**, 1913, **i**, 917).—Sphingomyelin has been prepared free from galactosides. It has the composition C = 64, H = 11, N = 3.40, P = 3.60, inorganic bases = 3 per cent. The ratio N : P = 2 : 1 (approx.). It contains no free amino-nitrogen. There are three methyl groups to two atoms of nitrogen, indicating that one of the methyl groups is in the form of choline. On hydrolysis the following substances are obtained:—phosphoric, lignoceric and cerobromic acids, choline, ergosine and another base having the composition $C_{13}H_{25}ON$.

H. W. B.

Specific Action of Enzymes considered from the Point of View of their Synthetic Power. EM. BOURQUELIER (*J. Pharm.* (Paris), 1914, [vii], **9**, 603—606).—A theoretical discussion in which the author points out the specific nature of various enzymes. Thus in an alcoholic solution of dextrose, β -alkylglucosides are alone formed under the influence of β -glucosidase, whilst α -alkylglucosides result from the same solution if α -glucosidase is employed. The mechanism of the change is discussed and the action contrasted with the action of zinc chloride on an alcoholic solution of dextrose or galactose.

The biochemical method is stated to be as advantageous as the ordinary chemical methods both in point of yield and purity of products.

H. W.

Inversion of Sucrose by Invertase. VIII. An Improved Method for Preparing Strong Invertase Solutions from Top or Bottom Yeast. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1914, **66**, 1566—1571).—The solution is prepared by well kneading 500 g. (10 kilos.) with tap water (10 litres) and toluene (500 c.c.) for three days, neutral lead acetate is added until precipitation is complete, the filtrate treated with hydrogen sulphide, filtered, and the filtrate at once thoroughly dialysed in collodion tubes, prepared from solution solutions of Pharmacopoeia strength in tubes 35×5 cm. The aged solutions are colourless and clear and show no loss in activity when kept, with toluene, for a month. At the end of a year the activity is reduced to about one-half. Both pressed top yeast and stem fermentation (brewers') yeast were employed. The latter yields extracts about twice as strong as the former. Liquefaction occurs in 8 hours and on the third day 5 c.c. of the filtered extract (from top yeast) was found to invert half the sucrose in 50 c.c. of a 9% solution, titrated with two drops of acetic acid and kept at 30° , in 5.9 hours.

The solution is without action on α -methylglucoside, maltose, and trehalose. Whilst a solution prepared from top yeast changed the rotation of a solution of raffinose from $+123^\circ$ to $+63.9^\circ$, a similar solution from bottom yeast changed the rotation from $+123^\circ$ to

+ 14.9%. This is attributed to the presence, in the solution from bottom yeast, of an enzyme (melibiose) which carried the hydrolysis of raffinose a step beyond that caused by invertase. N. H. J. M.

Inversion of Sucrose by Invertase. IX. Is the Reaction Reversible? C. S. HUDSON and H. S. PAINE (*J. Amer. Chem. Soc.*, 1914, 36, 1571—1581).—From the results of experiments in which various degrees of slight alkalinity and acidity were maintained a conclusion is drawn that invertase from yeast brings about the complete hydrolysis of sucrose to invert-sugar; that the reaction does not establish a mobile equilibrium, and is not a reversible reaction.

The results obtained by Osaka (A., 1908, i, 856) and by Vass (A., 1905, ii, 577) are attributed respectively to decomposition of levulose by hydrochloric acid and the known effect of hydrochloric acid on the rotatory power of levulose. The evidence afforded by the experiments of Kohl (A., 1910, i, 82) and of Pantanelli (A., 1912, 623) on the synthesis of sucrose by the action of invertase on cane sugar is considered to be doubtful. N. H. J. M.

Specific Nature of α -Glucosidase. A. ATTAY (*J. Pharmacol.*, 1914, [vii], 10, 23—26).—The main source of α -glucosidase is yeast which contains also maltase, and several authors therefore appear to consider that these substances contain the same enzyme although this conception is opposed to the work of Bourquelat and Hérissey (A., 1912, ii, 1104). The author has therefore investigated the question and is led to the conclusion that the two diastases are distinct.

Unsuccessful attempts to isolate maltase in the pure state from yeast are described: treatment of a maceration of yeast with 95% alcohol is found to destroy both maltase and α -glucosidase. Experiments have therefore been performed to determine whether the hydrolysis of maltose and α -methylglucoside occurs in parallel manner independently of the source of the maltase employed. Fresh human urine, after treatment with toluene, is found slowly to hydrolyse maltose but to be inactive towards α -methyl-glucoside; the quantity of maltase contained in it is, however, very small, whilst α -glucosidase appears to be completely absent.

A culture of *Aspergillus niger* on Rauvin's liquid, after being made with water, is known to yield a certain number of fermentations which is maltase, on contact with distilled water. Such a solution is found to hydrolyse maltose rapidly, whilst it is without action on α -methylglucoside. H. W.

Hydrolysis of Glycogen by Diastatic Enzymes III. Factors Influencing the End-point of the Hydrolysis. ROLAND VAN NOORDWIJK (*Biochem. J.*, 1914, 8, 421—433). Compare this vol., p. 121. Glycogen is not completely hydrolysed to maltose by pancreas diastase unless very high concentrations of enzyme are employed, although, even with low enzyme concentrations, the whole diastase glycogen may be changed into compounds of smaller molecular weight. The most important factor in retarding hydrolysis is probably

Liberating influence of the products of the reaction other than maltose. Evidence is adduced to show that neither the resistance of the dextrins formed to further hydrolysis nor the destruction of enzyme can account for the marked retardation of hydrolysis observed in the experiments.

H. W. B.

Constancy of the Optimum Temperature of an Enzyme under Varying Concentrations of Substrate and of Enzyme. ARTHUR COMPTON (*Proc. Roy. Soc.*, 1914, [B], 88, 258-262. Compare this vol., i, 215).—The temperature of optimum action of the enzyme of take-diastase is shown to be 47°, independent alike of the concentration of the substrate and that of the enzyme. E. F. A.

A Modification of Amygdalinase and Amygdalase Due to Iodine. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1914, 159, 434-436. Compare A., 1911, i, 825).—Working with the same preparation of amygdalinase and amygdalase from almonds, obtained in 1910 and kept in the dark in a well-stoppered flask, and measuring its activity and the reaction of the medium for optimum activity in December, 1910, July, 1912, and July, 1914, the authors find that not only do these enzymes lose their activity very slowly indeed, but they require an increasing optimum concentration of hydrogen ions with passage of time. W. G.

Enzyme Action. XXII. Lipase. IV. Correlation of Synthetic and Hydrolytic Activity. HENRY E. ARMSTRONG and T. W. GOSNEY (*Proc. Roy. Soc.*, 1914, [B], 88, 176-189. Compare 1913, i, 1120).—Parallel experiments have been made to ascertain the limits within which the opposing changes of hydrolysis and synthesis take place in presence of different proportions of the interacting substances and of water. Both in the case of the hydrolysis of olein by lipase and of its synthesis from oleic acid and glycerol, the rate and extent of the change is retarded as the proportion of water present is increased. In the hydrolytic change the water interferes directly by preventing the enzyme and the oil from coming into direct contact. In the synthetic change the water acts by withdrawing glycerol from the system through its dissolution, though synthesis is not entirely prevented in quite dilute solutions of glycerol.

During hydrolysis mono- and di-glycerides are at first produced, the net synthetic product being a diglyceride. The maximum synthesis observed was 40 per cent.

Burnet's observation (A., 1913, i, 920) as to the activity of the seeds of chelidonium is confirmed. E. F. A.

Physiological Chemistry.

Respiratory Exchange in Fresh-water Fish. I. Brown trout, JOHN ADDYMAN GARDNER and CONSTANCE LEETHAM (*Biochem. J.*, 1914, 8, 374-390).—A new apparatus for determining the respiratory exchange of fishes is described and illustrated.

The oxygen absorbed by brown trout (*Salmo Fario*) appears to be proportional to the temperature of the water in which they are placed, and is approximately doubled for an increase of 1° C. The average oxygen consumption is 102·5 c.c. per kilo. per hour at 4—7° and 206·5 c.c. per kilo. per hour at 16—17°. Large trout being warmed in water up to 25° quickly die, although the water is thoroughly oxygenated.

The average value for the respiratory quotient of brown trout is 0·81, but below 6° it falls suddenly to about 0·18, indicating a state of hibernation.

H. W. B.

The Blood in Acidosis from the Quantitative Point of View. W. McKIM MARRIOTT (*J. Biol. Chem.*, 1914, 18, 507—517; Compare A., 1913, ii, 450).—By means of a method differing slightly from that already described, the blood of normal young subjects, and of dogs, pigs, and cattle, has been found by the writer to contain less than 1·5 mg. of acetone and acetoacetic acid and less than 4 mg. of β -hydroxybutyric acid per 100 grams of blood, the results being expressed in terms of acetone. In acidosis the acetone substances in the blood are higher than normal. The highest figures obtained were 28 mg. of acetone and acetoacetic acid, and 45 mg. of β -hydroxybutyric acid per 100 grams of blood expressed as acetone.

H. W. B.

The Behaviour of the Sugar and Lactic Acid in the Blood Flowing from the Liver, after Temporary Occlusion of the Hepatic Pedicle. J. J. R. MACLEOD and A. M. WEED (*J. Biol. Chem.*, 1914, 18, 447—452).—The temporary arrest of the blood through the liver has been found by the authors to lead to an increase in the amount of sugar and lactic acid in the blood subsequently obtained from the vena cava. The increased proportion of these substances continues for at least fifteen minutes after the blood flow has been re-established.

H. W. B.

Effect of Haemorrhage and Re-injection of Blood and Saline Solution on the Vasomotor Centre. J. D. PILCHER and TORALD SOLLmann (*Amer. J. Physiol.*, 1914, 25, 56—62).—Haemorrhage progressively stimulates, depresses, and paralyzes the vasomotor centre. Re-injection of blood or saline solution into the onset of paralysis may restore the vasomotor tone. The level of blood pressure (systolic) level depends chiefly on the amount of blood lost, and not to an important degree on the rapidity of the haemorrhage.

H. W. B.

Effect of Intravenous Infusion of Normal Saline Solution on the Vasomotor Centre. J. D. PILCHER and TORALD SOLLmann (*Amer. J. Physiol.*, 1914, 25, 70—72. Compare preceding abstract).—In normal animals the intravenous infusion of 10—40 c.c. of saline solution per kilo. body-weight either slightly stimulates the vasomotor centre or leaves it altogether unaffected. In sick animals there may be considerable stimulation observed, which probably to be ascribed to a hypersensitive centre.

H. W. B.

Viscosity of Leaked Blood. RUSSELL BURTON-OPITZ (*Amer. J. Physiol.*, 1914, **25**, 51-58. Compare A., 1906, *i*, 372) —By repeated freezing and thawing of defibrinated blood the viscosity is first greatly increased and then very considerably reduced. Expressed numerically, the viscous resistance changes from being, when really defibrinated, 5.3 times greater than that of water at 37°, 14.1 times greater after eight freezings and thawings. This is accounted for by the fact that after the blood has been frozen from five to eight times the erythrocytes agglutinate and collect at the bottom and sides of the receptacle. The present determinations were made only with the liquid portion of the blood which remains relatively free from cells.

H. W. B.

The Clotting of Blood as Seen with the Ultramicroscope. C. H. HOWELL (*Amer. J. Physiol.*, 1914, **25**, 143-147). The author gives a description with photomicrographs of the phenomena observed under the ultramicroscope when solutions of thrombin are added to oxalated blood-plasma or to solutions of fibrinogen. The essential point is that the fibrin formed is deposited, not as a network, but as separate well-formed needles of crystalline appearance, which are massed to produce a mesh. In certain circumstances the process is incomplete, giving rise to the production of needles or rods of different lengths in place of the needles.

H. W. B.

Purine Metabolism of Rats. HAROLD ACKROYD (*Biochem. J.*, 1914, **8**, 434-437. Compare Folin and Morris, A., 1913, *i*, 925). The experiments recorded by the author show that the large amount of uric acid excreted by rats is an expression of a very great rate of purine metabolism, the main end-product of which is allantoin, beside which the amount of uric acid is insignificant. However, when hypoxanthine was given by the mouth to rats, over 60 per cent. of its nitrogen was excreted in the form of allantoin and only about 3 per cent. as purine nitrogen. The purine metabolism of rats is therefore like that of other lower animals, unlike that of man.

H. W. B.

Comparative Biochemistry of Purine Metabolism. I. and The Excretion of Purine Katabolites in the Urine of Arthropods, Rodents, Ungulates and Carnivora. ANDREW MILLER, MAURICE H. GIVENS, and CONNIE M. GEISS (with REUBEN S. MILLER and ALFRED OBERLE) (*J. Biol. Chem.*, 1914, **18**, 387-401, 416-428). Compare A., 1913, *i*, 126, 558; this vol., *i*, 348, 354, 378. A detailed account of work the results of which have already published (*loc. cit.*). H. W. B.

The Influence of Protein Intake on the Formation of Uric Acid. A. E. TAYLOR and W. C. BOSE (*J. Biol. Chem.*, 1914, **139**, 520).—By changing the nitrogen-free diet of a man fed for days on starch and sugar to one of white of egg containing less than 40 grams of nitrogen per diem (but no purines), the uric

acid output was raised from about 0·3 gram to 0·8 gram per kg., the creatinine nitrogen remaining unaffected. The possible explanations of this formation of uric acid on the heavy purine protein diet are discussed.

H. W. B.

Chemistry of Embryonic Growth. II. Comparative Analyses of the Eggs and of the Newly-hatched Larva of the Giant Salamander (*Cryptobranchus alleganiensis*). ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1914, **36**, 1518—1524. Compare *A.*, 1913, **i**, 673).—The eggs of *Cryptobranchus* contain two yellow pigments soluble in ether and in alcohol respectively. During development the eggs lose 1·66% of the dry matter. The amount of fat increases 14%; there is also a gain in the nitrogen soluble in ether and in the nitrogen soluble in alcohol (insoluble in ether). The total nitrogen is unchanged, and there is a loss of nitrogen from the protein fraction. Carbamide and uric acid are not produced in appreciable amounts.

It is considered probable that the eggs contain a carbohydrate nucleus, either free or in the form of a glucoprotein, which is broken down to carbon dioxide and water in the process of embryonic growth; and that the process proceeds more rapidly than required by the needs of growth, the surplus energy being stored as fat.

N. H. J. M.

Comparison of the Carbon Dioxide Output of Nervous Fibres and Ganglia in Limulus. SUTRO TASHIRO and H. E. ADAMS (*J. Biol. Chem.*, 1914, **18**, 329—334. Compare this vol., 1918).—The authors have determined the rate of evolution of carbon dioxide from the dorso-median cord in the heart of a king crab (*Limulus polyphemus*). It was found that about as much carbon dioxide was given off by this ganglionic nervous tissue as by the claw or optic nerves of the same animal. The amounts were considerably smaller than those furnished by the corresponding nerves of the spider crab (*Libinia canaliculata*), the frog (*Rana pipiens*), and this fact is correlated with the sluggish behaviour of *Limulus* and its power of living for long periods without food and with very little air. It is pointed out that the carbon dioxide output is directly proportional to the rate of propagation of the nerve impulse in these animals. Experiments so far recorded showing the influence of size and on the carbon dioxide output of nervous tissues do not allow any definite conclusion being drawn.

H. W. B.

The Effect of Acute Destructive Lesions of the Liver on its Efficiency in the Reduction of the Ammonia Content of the Blood. CYRUS H. FIRKE and HOWARD T. KARSKER (*J. Biol. Chem.*, 1914, **18**, 381—385. Compare this vol., **i**, 110).—The liver of animals which have been treated with chloroform, phloridzin, hydrazine, and haemolytic immune serum have been perfused with normal blood containing known amounts of ammonia. In each case the liver cells were able to remove 75%

by the whole of the ammonia, showing that the pathological changes induced did not interfere with the normal capacity of the liver to deal with ammonia.

During the progress of the work it was found that oxygenation of the perfusing fluid by pure oxygen instead of air brings about almost complete reduction of the ammonia content of the fluid as it passes through the liver.

H. W. B.

Ovarian Extirpation and Vasomotor Irritability. R. G. MACK and HOMER WHRELOX (*Amer. J. Physiol.*, 1914, **25**, p. 123. Compare this vol., i, 900).—Ovarian extirpation in rats results within six to eight weeks in a marked augmentation of the vasomotor reaction to nicotine, but not to adrenaline. These results, which are in conformity with clinical evidence, indicate that the operation causes a heightened irritability in the sympathetic nervous system.

H. W. B.

The Vapour Pressure Hypothesis of Contraction of Striated Muscle. H. E. ROOF (*Proc. Roy. Soc.*, 1914, [B], **88**, p. 159).—Starting with the commonly accepted structure for striated muscle, it is shown that it is possible to explain the phenomena associated with contraction on the hypothesis that lactic acid is set free in the muscle fibre, and that this combines with protein to form a salt with a consequent rise of osmotic pressure. As a result of this increased osmotic pressure the anisotropic bands swell and the muscle is thereby shortened. By various calculations, controlled by suitable experiments, it is shown that muscle can shorten by osmotic processes until its length is somewhere between 37% and 3% of its original length. From measurements of the elements of the sartorius muscle of the frog it is calculated that the amount of lactic acid formed during contraction of muscle can cause sufficient rise in osmotic pressure to account for the force exerted by the muscle and that the osmotic process can be completed in less than 0.04 of a second. The theoretical changes are also accounted for on the assumption of the formation of a protein salt of lactic acid.

H. W. B.

Creatine and Creatinine. PHILIP A. SHAFER (*J. Biol. Chem.*, 1914, **18**, 525—540. Compare Shaffer and Reinoso, A., 1910, ii, 1).—A detailed description of work the results of which have already been published (*loc. cit.*).

H. W. B.

Relations of Vitamine to Lipoids. EVELYN ASHLEY COOPER (*Chem. J.*, 1914, **8**, 347—354).—A method is described for the preparation from cardiac muscle of a substance small amounts of which cure polyneuritis in pigeons. The substance is extremely labile, and loses its activity in a few days. As in the case of heart muscle (A., 1913, i, 928), the bulk of the anti-neuritic substance contained in the fats and lipoids (alcoholic extract) of the muscle can be separated therefrom by means of ether. In the case of the brain, separation of the anti-neuritic substance is

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effected only by the addition of acetone as well as ether to the alcoholic extract.

Purified brain phosphatides, protagon, cephalin, cholesterol, cerebrin possess no curative power over polyneuritis. This is due to failure to become digested, because hydrolysed protagon and brain phosphatides are still quite inactive.

The conclusion is drawn that vitamine is not a lipid, although it may be adsorbed in the lipoids of the brain and nerves, it does not enter into their constitution, but is only stored as required by the organism.

H. W. B.

Colouring Matters in the Compound Ascidian *Diazoa violacea*. ALFRED HOLT (*Proc. Roy. Soc.*, 1914, [B], **88**, 227-238).—The Ascidian *Diazoa violacea* obtained by dredging near the Outer Hebrides is green while alive, but changes to violet when placed in alcohol, whilst the alcohol acquires the green colour. The spectrum of the green colour resembles that of ordinary green chlorophyll, and separable green and yellow pigments are associated in the alcoholic solution.

The violet substance, purified by solution in hot tetrahydroethane, formed a purple powder with a coppery lustre. In some behaviour it resembled the dibromoindigotin shown by Kellander to be present in *Murex brandaris*. The same dibromoindigotin has now been isolated from the British murex *Purpura lapillus*.

It is considered that in the healthy animal the purple pigment is present in its reduced condition as a colourless chromogen, and is physiologically active as an oxygen carrier. On death, oxidation is complete, and the violet pigment persists.

E. F. A.

The Validity of the Microchemical Test for the Oxygen Place in Tissues. A. N. DRURY (*Proc. Roy. Soc.*, 1914, [B], **88**, 166-176).—Experiments have been made by the author to prove that the results obtained by Unna with rongalite—a solution of the leuco-base of methylene-blue kept in a state of reduction by excess of rongalite (formaldehydesulphoxylate)—justify his assumption that it is a specific stain for the oxygen place in tissues; consequently, his theory of staining by oxidation and reduction is not proven. Experiments were also performed which showed that the gas condensed on the surface is a factor in determining the depth to which staining takes place. Altering a surface by preliminary treatment with various organic substances also has a marked effect on the subsequent condensation of methylene-blue.

H. W. B.

Biochemistry of Iodine. I. The Distribution of Iodine in Plant and Animal Tissues. A. T. CAMERON (*J. Biol. Chem.*, 1914, **18**, 335-380).—The author has estimated the amount of iodine present in various animal and vegetable tissues by a modification of Hunter's method (A., 1910, ii, 650). The results are compared with those obtained by other workers.

Iodine has been found in the great majority of plants, the exact amount present being largely dependent on the amount of iodine in the environment. Marine algae usually contain more than 0·1% of iodine, whereas in fresh-water algae and vegetables the quantity is generally less than 0·0001%. Nevertheless, distinct variation of iodine content can occur in the same species growing under apparently the same conditions. A possible explanation is based on Allary's statement (which is confirmed) that when a part of one of the marine algae ceases to grow and commences to lose its vitality, it gives up iodine to the surrounding medium.

Among the lower animals, sponges were found to contain about 0·1% iodine (calculated on the dried material), whilst worms contained up to 0·4%. In all the lower animals the iodine is dispersed throughout the various tissues of the organism, but in the higher animals it becomes concentrated in the thyroid, so that in vertebrates this gland is the only tissue containing more than a trace of it. In thyroid tissue marked variations of iodine content can both in individuals of the same species and in different species. Such variations are all traceable to differences in diet, i.e., vertebrates the amount of iodine in the dried thyroid varies from 0·01 to 1·16%.

Iodine is present in the thyroids of the young of sheep, swine, and cattle to a rather greater extent than in the adult animal. The iodine content of the parathyroids is of an altogether lower order than that of the thyroid. The remaining tissues, including lungs and pituitary, of the cat, dog, and rabbit do not contain more than a trace of iodine (less than 0·001% calculated on the dried material).

H. W. B.

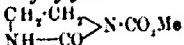
Relative Amounts of β -Hydroxybutyric Acid and Acetoacetic Acid Excreted in Acetonuria. ERNEST LAURENCE KENNARD (*Proc. Roy. Soc. (Biol.)*, 1914, **8**, 355—365).—The author has estimated the relative amounts of β -hydroxybutyric acid and acetoacetic acid in urine in conditions of acidosis. In diabetes the ratio of hydroxybutyric acid to acetoacetic acid remains fairly constant; during carbohydrate starvation, the proportion of β -hydroxybutyric rises with the increasing formation of acetone substances. In cases where two and a half grams or more of the two acids were excreted daily, the estimation of the separate acids indicated that from two to five molecules of β -hydroxybutyric acid were excreted for one molecule of acetoacetic acid.

H. W. B.

The Behaviour of Asparagine, Phenyl Carbamate and Methyl Ethyleneallophanate [Methyl Glyoxalidone-1-carboxylate] in Phloridzin Diabetes. OTTO NIRSCHE (*Chem. Zentr.*, 1914, **6**), from *Beitr. Phys.*, 1914, **1**, 53—89.—The author records effects on the urinary sugar of the administration of L-asparagine, phenyl carbamate, and methyl glyoxalidone-1-carboxylate to undiabeticated dogs. From the quantity of "extra" sugar (Lusk) found after the ingestion of asparagine, the author infers that

three of the carbon atoms in asparagine become transformed into dextrose. The administration of 3 grams of phenyl carbamate in one dose to a phloridzinised dog caused the death of the animal, whilst a dose of 1 gram resulted in a diminished elimination of sugar.

[With NUSSHAG.]—*Methyl glyoxalidone-1-carboxylate,*



has been prepared from ethylenedicarbimide and methyl alcohol in crystalline form, soluble in water and alcohol. A 10 gram dose did not produce narcosis. Administration to a phloridzinised dog led to an increase in the urinary dextrose. H. W. B.

Formation of Dextrose from Glutamic Acid in Phloridzin Diabetes. BRUNO WARKALLA (*Chem. Zentr.*, 1914, ii, 601—61; *Beitr. Phys.*, 1914, 1, 91—112. Compare Lusk, A., 1908, 1, 85).—The administration of glutamic acid, obtained from the grain of wheat, to phloridzinised dogs leads to an increased elimination of dextrose in the urine. The calculation of the "extra" sugar from the D : N ratio does not enable it to be decided whether an intermediate compound formed during the transformation of glutamic acid into sugar possesses three or only two carbon atoms. H. W. B.

The Behaviour of Certain Amido-compounds in Phloridzin Diabetes. KARL STEINHAUSEN (*Chem. Zentr.*, 1914, n. 1; *Beitr. Phys.*, 1914, 1, 113—142).—The author has determined the influence of the administration of succinimide, succinamide and acetamide to phloridzinised dogs on the elimination of sugar in the urine. The experiments carried out on a fasting rabbit show succinimide did not give a conclusive result, but those on a fasted dog showed unmistakably that what Lusk has termed "extra" sugar was eliminated. After the ingestion of 40 grams of acetamide, about 30 grams were obtained during the next three hours unchanged from the urine, leaving only 10 grams to take part in metabolism. The author does not come to any conclusion as to whether the "extra" sugar formed in this experiment arises from gluconeogenesis from the ingested acetamide. The administration of succinamide interrupts the normal course of phloridzin diabetes so that no statement as to its capacity for being utilised as sugar can be given. H. W. B.

The Behaviour of Acrylic Acid in Phloridzin Diabetes. FRIEDRICH SCHWENKEN (*Chem. Zentr.*, 1914, ii, 254; from *Beitr. Phys.*, 1914, 1, 143—177).—The author advances the hypothesis that acrylic acid may be an intermediate product between lactic acid and alanine on the one hand and dextrose on the other. The administration of acrylic acid to phloridzinised dogs led to an increase in the amount of dextrose eliminated in the urine. The loss of urinary dextrose over that occurring in the urine before acrylic acid was given to the animal was such as to lead the author to

surer that all the acrylic acid administered had been converted into dextrose. The formation of dextrose in the body from lactic acid or alanine may therefore occur with acrylic acid as the intermediate product.

H. W. B.

Magnesium Narcosis. I. E. STARKENSTEIN (*Chem. Zentr.*, 1914, 59, from *Zentr. Physiol.*, 1914, **28**, 63—70). In order to determine whether the point of attack of magnesium salts is in the central or peripheral nervous system, the author has carried out a number of "combination" and "antagonistic" experiments on rabbits. Camphor, which has an antagonistic action on the central aldehydes and chloral narcosis, has no action on magnesium narcosis. Eserine has a stimulating action on magnesium narcosis similar to that exerted on the peripheral paralysis brought about by curare; the paracetaldehyde and chloral narcosis of central origin remain unaffected. Eserine calls forth muscular tremor in normal and curarised rabbits, but not in animals narcotised by magnesium, paracetaldehyde, or chloral. Phenol in small doses shares in the same way as eserine.

Infective doses of curare and ether when combined may bring about complete narcosis. Magnesium and ether have similar additive effects.

In view of these results, magnesium narcosis cannot be said to indicate either a purely central or a purely peripheral paralysis. It appears, rather, that all parts of the nervous system are rendered inexcitable by the magnesium ions. The experiments also show that the action of the other drugs is not confined exclusively to the central or the peripheral nervous system, and that even when there is a pronounced peripheral action (as with curare), there may be a considerable central paralysis.

The intensifying action of oxalates on magnesium narcosis noted by Gates and Meltzer (this vol., i, 459) has already been described by the author (*Wien. Klin. Woch.*, July, 1913).

H. W. B.

The Parenteral Utilisation of Disaccharide Sugars. ALBERT HECHT (*J. Biol. Chem.*, 1914, **18**, 485—496). Repeated injections of lactose and sucrose have been made into the intraperitoneal cavity of dogs. Most of the injected sugar has been regained from the urine. Greater utilisation of these sugars could not be attained by repeated injections. These experiments, therefore, do not yield confirmation of Abderhalden's work showing the development of enzymes by the organism capable of hydrolysing these sugars when parenterally introduced.

H. W. B.

Action of Tissues on Methyl-glucosides, Tetramethyl glucosides and Natural Disaccharides. P. A. LEVENE and G. M. IRVING (*J. Biol. Chem.*, 1914, **18**, 469—475).—An attempt has been made by the authors to trace the changes undergone by the dextrose molecule during its oxidation in the body by studying the action of the tissues, taken post-mortem, on derivatives of dextrose. Sliced rabbit kidneys were incubated for thirty-six hours with solutions

of α -methyl-glucose, tetramethyl-glucose, sucrose, lactose, *d*-glucose, phosphoric acid, maltose, and β -methyl-glucose. In all except the last two, no change in the reducing power of the solution, taken before and after hydrolysis, was observed. With maltose and β -methyl-glucose slight change occurred, due doubtless to the preliminary cleavage of these substances into their components by the tissue enzymes. The conclusion drawn is that only *d*-dextrose undergoes oxidation in the body, ester and ether derivatives of dextrose being unaffected. H. W. B.

The Changes Undergone by Salicylic Acid in the Animal Organism. ALESSANDRO BALDONI (*Chem. Zentr.*, 1914; **i**, 2066; *Arch. Farm. sperim.*, 1914, **17**, 241—247. Compare A., 1908, **i**, 1000).—A critical consideration of the method of isolation and properties of the hydroxysalicylic acid obtained by Neuberg (*Bioch. Woch.*, 1914, **48**, 798) leads the author to the conclusion that it is possible that this substance is identical with the salicylic acid which he prepared from human urine after administering sodium salicylate (*loc. cit.*). H. W. B.

Uricolysis. A. E. TAYLOR and W. H. ADOLPH (*J. Biol. Chem.*, 1914, **18**, 521—523).—A large quantity of allantoin was injected into the femoral vein of a dog and recovered almost quantitatively from the urine with no concurrent increase in the elimination of urea. In the dog, allantoin is not converted into urea, and therefore it is probable that in man the corresponding conversion of uric acid into urea does not take place. H. W. B.

Chemistry of Vegetable Physiology and Agriculture

Mechanism of Agglutination of Bacteria by Specific Serums. WILLIAM JOHN TULLOCH (*Biochem. J.*, 1914, **8**, 293—319).—The author has investigated the factors determining the flocculation of sensitised bacteria, and expresses the view that whereas unsensitised organisms exhibit characters that are similar to those of protein sensitised organisms recall in their properties the characteristic features of denatured protein.

Specific agglutination is markedly affected by the presence of salts, hydrogen- and hydroxyl-ions. In the presence of salts or mono- and bi-valent cations, unsensitised bacteria behave like rigid colloids, such as egg-albumin, but after they have been sensitised they resemble rigid colloids (denatured egg-white). Flocculation appears to be due to a direct interaction of the substance-antigen complex with the electrolyte. Both hydrogen and hydroxyl-ions inhibit agglutination by interfering with

ence of antigen with anti-substance as well as by preventing flocculation.

The agglutinating activity of an electrolyte depends on the agency of its cation when the bacteria are suspended in saline solution, and on the valency of the anion when suspended in a acid medium. Salts with multivalent cations are peculiar in their action in that they are as active in the precipitation of sensitised as of unsensitised organisms. Since flocculation takes place in the presence of fluorides, agglutination is independent of the divalent ions in the serum.

The general conclusion arrived at is that the process of sensitisation is akin to denaturation. H. W. B.

Studies in Bacterial Metabolism. XXXI—XXXVII. ARTHUR KENDALL, ALEXANDER A. DAY, and ARTHUR W. WALKER (*J. Amer. Chem. Soc.*, 1914, **36**, 1937—1962).—An investigation of the effect of various important types of bacteria on milk. Estimations were made of the free ammonia, total nitrogen, and the acidity or alkalinity as indicated by alizarin, neutral red, and phenolphthalein. As certain changes, particularly increases in acidity, were observed which could not be adequately explained, experiments were undertaken with a view to determine the effect of butter-fat on the bacterial metabolism. For this purpose, skimmed milk containing 0·15% of butter-fat, whole milk (containing 3·6% of butter-fat), and cream (containing 40% of butter-fat) were inoculated with certain organisms and studied under parallel conditions. The results of all these experiments are tabulated. E. G.

Studies in Bacterial Metabolism. XXXVIII. ARTHUR L. KENDALL, ALEXANDER A. DAY, and ARTHUR W. WALKER (*J. Amer. Chem. Soc.*, 1914, **36**, 1962—1966).—A study of bacterial metabolism in milk (preceding abstract) showed the occurrence of certain changes, chiefly in relation to acidity, which could not be explained in the information hitherto available. In seeking an explanation of these changes, experiments have been carried out to ascertain whether the organisms secrete lipases which effect the hydrolysis of the fatty constituents of the milk. The results show that the culture filtrates of broth cultures of certain bacteria are capable of hydrolysing butter-fat, ethyl butyrate, and triacetin. E. G.

Action of Stimulants on Nitrifying Bacteria. C. MONTANARI (*Chem. Zentr.*, 1914, ii, 342; from *Staz. speriment. agrar. Ital.*, **47**, 81, 449).—The results of experiments with manganese dioxide, nitrate, and sulphate showed that manganese dioxide and carbonate rendered nitrification more vigorous. N. H. J. M.

Action of Organic Substances on Nitrification and Denitrification in Soils. ALEXANDER Kosowicz (*Chem. Zentr.*, 1914, ii, 260—261; from *Zeitsch. Gärungsphysiol.*, 1914, **4**, 1—48).—The results of experiments on nitrification in a soil rich in humus proved that straw only had a retarding action when employed in

very large amounts, and that straw plus peptone had less effect than peptone alone.

Denitrification is greatly accelerated by straw. Straw plus peptone acts similarly. This is followed by a vigorous nitrification of the ammonia produced from the peptone.

The retarding effect of the following substances on nitrification decreases in the following order: peptone, asparagine, acetamide, ammonium acetate, and carbamide. When peptone is added, nitrification and denitrification only commence when all the nitrogen of the peptone is converted into ammonia; production of nitrate and of nitrite nearly always begin simultaneously. The effect of dextrose is similar. In presence of soluble organic compounds nitrification does not proceed until they are completely mineralized.

N. H. J. M.

Chemical Nature of a Bacterial Haemolysin. ERIC ELLIS ATKIN (*Biochem. J.*, 1914, 8, 328-346).—The velocity of destruction of *Vibrio nasik* haemolysin, prepared from *Vibrio nasik*, at 46° is at a minimum slightly on the acid side of the neutral point. This favours the view that the lysin is an amphotelyte (ampholyte or trolleyte) with its acid dissociation constant greater than its base and the point of minimum destruction is the isoelectric point. The anion and cation are therefore thermolabile, and the dissociated molecules thermostable. Kataphoresis experiments at 37° confirm this view. The approximate values for the isoelectric points are p_{H^-} at 10° = 3.3; p_{H^+} at 46° = 6.1. This decrease of value with rising temperature is also found in the case of simple amphotelytes, but to a smaller extent.

A criterion is also given incidentally for the anomalous local destruction of certain haemolysins, for instance, megathermous, namely, that the process is not unimolecular at temperatures where the velocity of destruction decreases with rising temperature, but can be shown to be so at temperatures considerably removed where the velocity of destruction follows the more ordinary course of increase with rise of temperature.

H. W. B.

Combination of Metallic Salts by Yeast; their Detection by Chemical Reactions. TH. BOKORNY (*Chem. Zentr.*, 1914, 2195-2196; from *Allgem. Brauer-Hopfenzeit.*, 1914, 54, 1135-1138).—Pressed yeast (20 grams) fixes 0.25 gram of copper sulphate two weeks from a 1% solution; the yeast gives a positive reaction with potassium ferricyanide. Yeast-ferrous sulphate only reacts with potassium sulphide and potassium ferro- and ferricyanide after being boiled with hydrochloric acid. Yeast-ferric chloride also gives mostly negative reactions, except with ammonium sulphide. The compound with cobalt nitrate gives mostly negative reactions, whilst nickel sulphate seems to be incompletely fixed and manganese sulphate not at all. The compounds with mercuric salts only give positive reactions with ammonium sulphide, whilst the compound with lead acetate gives a negative reaction. Sodium hydrogen sulphite enters into

reaction with the aldehyde of the active protein; when treated with dilute sulphuric acid, it liberates sulphur dioxide.

N. H. J. M.

Yeast Fermentation and Hydrogen. SERGIUS LVOV (*Chem. Zentr.*, 1914, i, 2194—2195; from *Zeitsch. Garungsphysiol.*, 1913, 3, 39—320).—Experiments on the action of chromogens, the fermentation of sugar, and the autofermentation of yeast. The vegetal pigments examined probably contain a double linking, which can unite with two atoms of hydrogen, with production of new compounds. The process proceeds readily in presence of yeast reductase, for example. In leuco-compounds the hydrogen is in loose combination, and is oxidised to water by molecular oxygen. One gram-mol. of methylene-blue withdraws from the fermenting medium 1 gram-mol. of hydrogen, and renders 1 gram-mol. of hexose inactive, and thus prevents the further decomposition into alcohol and carbon dioxide.

As regards the autofermentation of yeast, 1 gram-mol. of methylene-blue causes the production of an excess of carbon dioxide (1 gram-mol.); that is to say, the fermenting medium contains a substance which, in absence of sugar, gives up 1 mol. of carbon dioxide, two hydrogen atoms being removed from the substance. This is an enzymatic process which does not take place if the yeast is destroyed by heat. The carbon dioxide presumably comes from the fermentation of amino-acids, with production of dihydrides.

Reducتase has the most important share in the fermentation processes by activating hydrogen.

N. H. J. M.

Assimilation of Nitrates by Moulds. ALEXANDER KOSOWICZ (*Chem. Zentr.*, 1914, i, 2192; from *Zeitsch. Garungsphysiol.*, 1913, 3, 31—326. Compare 1913, i, 571).—Whilst it is shown that moulds can assimilate nitrates directly, without previously converting the nitrate into ammonia, some moulds, when well developed, produce ammonia in solutions of nitrates. The production of ammonia in such cases is attributed partly to the reducing power of the mature moulds and partly to the decomposition of nitrogenous organic constituents of the moulds.

N. H. J. M.

Germination and Growth of Some Plants and Nitrification in Presence of Naphthalene. P. CAICCIARI (*Chem. Zentr.*, 1914, ii, 53—54; from *Stat. sper. agrar. Ital.*, 47, 347—367).—Considerable amounts of naphthalene are without effect on the germinating power of seeds; the energy of germination is, however, somewhat affected, and growth is retarded. Naphthalene is unfavourable to nitrification.

N. H. J. M.

Photosynthetic Processes in Green Plants. E. SERRAGIOTTO (*Vaccetta*, 1914, 44, i, 628—631. Compare this vol., i, 1121).—As described in the paper referred to, the author's efforts to obtain free methylene yielded, instead, unsaturated and cyclic polymerides

of it. He suggests that the initial reaction in the photosynthetic processes of green plants may be $\text{CO}_2 + \text{H}_2\text{O} = \text{O}_2 + (\text{CH}\cdot\text{OH})_n$, and that the hydroxymethylene so formed then polymerises. A typical cyclic polymeride would be $(\text{CH}\cdot\text{OH})_6$, which is ionised, and is widely distributed in plants. Schemes are given showing the formation of other products from the original polymeride, and changes identical with, or similar to, reactions which have been observed under laboratory conditions.

R. V.

Partition of the Nitrogen of Plant, Yeast and Meat Extracts. F. C. COOK (*J. Amer. Chem. Soc.*, 1914, **36**, 1551—1554). Comparing the amounts of nitrogen precipitated by different reagents in the various extracts, it was found that phosphotungstic acid precipitated the highest, tannin salt the next highest, acid-alcohol the lowest percentage of nitrogen. Sørensen's urealdehyde titration method gave lower results for amino-nitrogen than the Van Slyke method.

The results showed that more of the nitrogen is present in a more completely hydrolysed state in plant extracts than in yeast and meat extracts. Plant and yeast extracts were found to contain no creatine and creatinine; the former contains very little nitrogen as purine, whilst the latter showed high purine nitrogen. Only meat extracts showed the biuret reaction.

The nitrogen of plant extracts consists chiefly of inorganic acids and ammonia, none of it being precipitated by acid-alcohol. In the case of meat and yeast extracts, about 25% of the nitrogen is precipitated by acid-alcohol.

N. H. J. Y.

Colouring Matter contained in the Seed-coats of *Abrus precatorius*. SARASI LAL SARKAR (*Biochem. J.*, 1914, **8**, 281—294).—The outer layer of cells of the seed-coats of *Abrus precatorius* is impermeable to water and other solvents, so that if a batch of seeds is thrown into water, the colouring matter is dissolved only out of those which may have become ruptured, the entire seeds retaining their colour.

On soaking the crushed seed-coats in water, two colouring matters, yellow and scarlet, are extracted, and can be separated by shaking with ether. The scarlet colouring matter, which is the chief one present, remains dissolved in the water, and can be purified by means of its insoluble copper salt. Its reactions with ferric chloride, gelatin, ammonium ferricyanide, etc., indicate that it is a tannin substance.

Observation of microscopical sections of the seed-coats of *Abrus precatorius* treated with the above reagents showed that the scarlet colouring matter is located in the outermost layer of cells, whilst the yellow pigment is contained in a layer of cells situated at some distance from the surface of the seed-coat.

H. W. B.

Anatomy and Microchemistry of *Anacardium occidentale*. ERNST KRATZMANN (*Chem. Zentr.*, 1914, ii, 244; from *Pharm. f. d.* 1914, **47**, 375—378).—Cardol and anacardic acid, an oily substance

and crystals, m. p. about 117°, were separated. The seeds contain considerable amounts of fat, besides much starch. N. H. J. M.

Chemical Examination of Cotton root Bark. FREDERICK B. POWELL and HERSEY BROWNING, jun. (*J. Pharm. J.*, 1914, 93, 420—43).—On distilling an alcoholic extract of cotton root (*Gossypium herbaceum*) bark with steam, a very small amount of a pale yellow, essential oil is obtained. The product gives the colour reaction of furfuraldehyde, and, by keeping, deposits a few crystals, m. p. 112—114°, which appear to consist of acetovanillone. The other constituents of the bark are found to comprise: (1) a phenolic acid, m. p. 126—129°, which is probably 2,3-dihydroxybenzoic acid; (2) salicic acid; (3) a colourless, phenolic substance, $C_9H_{10}O_3$, m. p. 125—264° (acetyl derivative, m. p. 152°), which forms yellow cations in aqueous alkalies, and develops a purple coloration with ferric chloride; (4) a yellow, phenolic substance, $C_{13}H_{14}O_5$; (5), m. p. 210—212° (acetyl derivative, m. p. 147—149°), which develops a deep purple coloration with aqueous alkalies and with concentrated sulphuric acid, and a brown coloration with ferric chloride; (6) betaine; (6) a fatty alcohol, $C_{20}H_{42}O$, m. p. 77.5—78.5°; (7) a phytosterol, $C_{28}H_{46}O$, m. p. 130°; (8) a small amount of a tricarboxylic triacontane (I), m. p. 60—61°; (9) ceryl alcohol; (10) a mixture of fatty acids, consisting chiefly of oleic and palmitic acids; and (11) a considerable proportion of sugar, from which *d*-phenylglucosazone and penta-acetylhexose have been prepared.

The bark does not contain any alkaloid or tannin. The gummy component, from which some of the substances mentioned here are isolated, has a deep purple colour, and amounts to 10% of the weight of the air-dried bark employed. C. S.

Presence of Gentiopicrin and Gentianose in the Fresh Roots of *Gentiana purpurea*, L. MARC BRIDEL (*J. Pharm. Chim.*, 1914, viii, 10, 62—66. Compare A., 1913, i, 149, 150, 434, 435, 436, 1212).—The author has previously examined a cultivated specimen of *Gentiana purpurea*, L., and now gives the results of investigation of the wild plant, which is found to contain about twice as great a quantity of substances hydrolysable by invertin as emulsin as the cultivated specimen. Further evidence of the presence of an unknown sugar, hydrolysable by invertin, is also obtained. The roots of *Gentiana purpurea*, L., appear to be very similar in composition to those of other gentians previously tested, and, on extraction, yield crystallised gentiopicrin, $[\alpha]_D -196.6^{\circ}$, and gentianose, $[\alpha]_D +31.43^{\circ}$, the proportion of the latter being identical with that contained in the yellow gentian. H. W.

Biochemical Investigation of the Glucosides, Hydrolysable by Emulsin, in Indigenous Orchidaceæ. EM. BOURQUELOT and J. BRIDEL (*J. Pharm. Chim.*, 1914, [vii], 10, 14—18, 66—72).—The method is as follows. The fresh plant is introduced in portions

into boiling 85% alcohol, and ebullition continued for fifteen to twenty minutes to ensure the destruction of all ferment. After cooling, the extract is decanted, and the residue again heated in alcohol. The united alcoholic liquors are filtered and evaporated, and the residue dissolved in water containing thymol. The rotation of the liquid is determined, reducing sugar is estimated, and invertase added. Sucrose, if present, is thereby hydrolyzed, and the rotation changes towards the levo-direction. When no further change in rotation is observed, the liquid is heated at 100°. After cooling, emulsin is added. Should the plant contain a hydrolysable glucoside, the rotation returns towards the right, the extent being proportional to the amount of glucoside in solution.

The orchidaceæ examined are divisible into two groups. Those belonging to the series *Aceras*, *Loroglossum*, *Orchis*, *Ophrys*, or *Platanthera* yield dextrorotatory extracts; the others, comprising the species *Limodorum*, *Cephalanthis*, *Epipactis*, and *Nectria*, give levorotatory extracts. All species contain a sugar hydrolysable by invertase. In most cases, sucrose is in all probability present, the most marked exception being presented by *N. Nidus-avis*. All the plants contain one or more glucosidic substances hydrolyzable by emulsin, which possibly vary in the different cases. Nevertheless, for the majority of species, the indices observed lie within moderately close limits, which points to the presence of the same glucosidic principle in each, and the fact that a precipitate always separates during the action of emulsin lends support to this view.

H. W.

Occurrence of Manganese in Kentucky Soils and its Possible Significance. O. M. SUZNO (*J. Ind. Eng. Chem.*, 1914, 6, 600-633).—Although manganese is universally present in soils and plants, there are large differences in the manganese content of the soils of different geological areas, and sometimes in those from the same area. The amounts found in the surface soils examined range from 0.005 to 0.331% (MnO), and in the subsoils from 0.005 to 0.264%. Usually, the surface soils contain the larger amounts, less manganese is found in cultivated soils than in the corresponding virgin soils; the same holds good in the case of the crops. Most soils contain considerably more manganese than phosphorus, but the loss of manganese from cultivated soils is greater than that of phosphorus. The application of certain manganese salts, particularly the sulphate, to soils is beneficial to the crops, but quantity applied must, however, be small, as large quantities are harmful.

W. P. S.

General and Physical Chemistry.

Wave-lengths of Hydrogen Lines and Determination of μ Series Constant. W. E. CURTIS (*Proc. Roy. Soc.*, 1914, [A], 90, 55-620).—The wave-lengths of the first six lines in the series spectrum of hydrogen have been measured with the greatest possible accuracy in order to determine the exact relationship between the wave-lengths of the series lines. The accuracy gained is of the order of 0.001 Å, but the actual accuracy depends on the time of exposure, increasing with the length of this period in consequence of changes in the temperature of the instrument.

The results obtained show that Balmer's formula does not afford an exact representation of the relation between the wave-lengths of the various lines. The numbers can, however, be accurately represented by a modified Rydberg formula, $n = N/4 - N/(m + \mu)$, which $N = 109679.22$ and $\mu = 0.069$. This formula gives the emergence frequency of the series as 27419.805, corresponding to a wave-length (in air) of 3645.981 international units. Up to the present, the Balmer series of hydrogen lines has usually been regarded as of the diffuse type. It is suggested that in this case the sharp and diffuse series practically coincide, and that the Balmer series represents the superposition of the two.

H. M. D.

Absorption Spectrum of Zinc Vapour. J. C. McLENNAN (*W. Mag.*, 1914, [vi], 28, 360-363).—It has been found that zinc vapour shows an absorption band at $\lambda 2139.33$, but no evidence of absorption at $\lambda 3075.99$ was obtained even at the highest temperatures employed in the experiments. The three lines, mercury $\lambda 1849.6$, cadmium $\lambda 2288.79$, and zinc $\lambda 2139.33$, are homologous and correspond with a value of $m = 2$ in Paschen's single π series, $n = 1.5$, $N = mP$. It is probable that these series of lines is to be attributed to atoms of the respective metals in the atomic state.

H. M. D.

Absorption Spectra at Very Low Temperatures. ARRIGO MECCHELLI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 953-959).—In view of the fact that the bands of the phosphorescence spectra of metal salts become narrower and more clearly defined at very low temperatures, the author has investigated the absorption spectra of methyl sulphate, chloride, bromide, iodide, and *o*- and *p*-hydroxybiphenyls at temperatures somewhat above -180°. At such temperatures solutions of the salts in ethyl alcohol solidify to transparent glassy masses suitable for observation; addition of glycerol to the ethyl alcohol lowers the solidifying point considerably, but the solutions then give either an opaque mass or a transparent one, which rapidly disintegrates. The absorption

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bands are found to become clearer, and to be appreciably displaced at the low temperatures used; in some cases new bands make their appearance.

Examination of various colouring matters in the same manner shows that at about -180° the absorption bands differ but very slightly in position and clearness from those observed at ordinary temperatures. It seems, therefore, that the influence of low temperatures on the absorption bands is pronounced only with compounds, the selective absorption of which is a property of the constituent elements.

T. H. P.

Action of Radium Emanation on Explosive Gas. Schurz (Compt. rend., 1914, 159, 423—426). Compare this work (649).—Hydrogen and oxygen readily combine under the influence of radium emanation, and in one case the combination was accompanied by an explosion. The products of the reaction are water and hydrogen peroxide, the water probably being formed as a decomposition product of the hydrogen peroxide. No oxygen can be detected, and but little is formed when working with water alone under the same conditions (compare Lind, A., 1911, 1, 11).

W. G.

Immutability of the Uranium Radiation. W. P. Jones and J. A. Volterraff (Chem. Weekblad, 1914, 11, 852).—Exposure to cathode rays produces no change in the uranyl uranoso-uranic oxide. The increase noted by Jorissen and Regnaut (A., 1907, ii, 422, 731) was due to changes in the surface area of the preparations employed.

A. J. W.

Electrification at Liquid-Gas Surfaces. H. A. McLeod (Phil. Mag., 1914, [vi], 28, 367—378).—The velocity with which bubbles of air move through various liquids under the influence of an electric field has been examined in a series of experiments with aqueous solutions of various alcohols and fatty acids. In particular, the dependence of the velocity on the size of the bubbles and on the concentration of the solution was investigated.

The addition of alcohols (or fatty acids) reduces the size of the bubbles, and therefore the electrification at the liquid surface, the effectiveness of any alcohol in this respect decreasing with its effectiveness in reducing the surface tension of water. This reduction of surface tension is caused by a positive adsorption of alcohol into a surface layer of small thickness. The latter difference between the velocities for pure water and a given alcohol diminishes as the diameter of the gas bubble decreases, and that the degree of adsorption is dependent on the curvature of the surface. At the moment of disappearance of the bubble, the concentration of the surface layer is equal to that of the surrounding solution.

Experiments with air bubbles in pure alcohols show that there is no electrification at the surface of contact with the liquid. All other evidence indicates that the electrification phenomena

observed in "water-fall" experiments are not due to the potential differences which come into play in the cataphoresis experiments.

H. M. D.

Emission of Electric Charges by Salts Non-radioactive at the Ordinary Temperature. D. PACINI (*Nuovo Cim.*, 1914, [vi], 7, i, 267—290).—Further study of the phenomenon already described by the author (A., 1907, ii, 475) and others with ammonium, sodium, potassium and barium sulphates, ammonium nitrate and potassium bromide gives results which indicate that the property of emitting electric charges is to be attributed to the action, probably an electrochemical one, of water-vapour on these salts. The charges seem to be carried by ions, and the hypothesis is advanced that the phenomenon is one of molecular dissociation, the nucleus of the predominating positive ions being an atom of the metal or, more probably, one of hydrogen generated by the dissociation of the water-vapour. The effects of change of pressure, temperature, and intensity of field were studied. Indications of a "fatigue" of the phenomenon could not be corroborated.

T. H. P.

Conductivity of Salt Vapours. S. J. KALANDYK (*Proc. Roy. Soc.*, 1914, [4], 90, 634—647).—The conductivity exhibited by the vapours of the halogen salts of zinc and cadmium has been investigated. It is shown that the conductivity is mainly due to processes occurring in the vapours themselves, and is practically independent of the emission of charges from the surface of the heated salt. The vapours of carefully dried salts exhibit marked conducting power, though this is greatly increased in the presence of water-vapour. The greatest increase was observed in the case of zinc iodide, which is the most hygroscopic of the substances examined.

Although previous experiments (compare Garrett, A., 1907, ii, 16) have shown that in ordinary circumstances the conductivity of the salt vapour seems to vary with the duration of the treatment, the author has found that carefully dried cadmium oxide gives rise to a steady current.

The connexion between the current i and the temperature θ can be expressed with considerable accuracy by the formula $i = a \cdot e^{-b/\theta}$, in which a and b are constants. On the assumption that the conductivity is due to the ionisation of the vapours, the ionising potential has been calculated with the following results: cadmium iodide, 3.1; zinc iodide, 2.72; zinc bromide, 2.97 volts. These values are much smaller than the corresponding ionising potentials for the diatomic gases.

From experiments with phosphorus pentabromide and sulphur chloride it has been found that these vapours are non-conducting. From this it follows that ionisation is not a consequence of chemical reaction.

H. M. D.

Dissintegration of the Aluminium Cathode. L. L. CAMPBELL (*Proc. Roy. Soc.*, 1914, [vi], 28, 347—354).—It has been supposed that the

aluminium cathode does not disintegrate to any marked extent except in the presence of the inert gases, but this view is shown to be untenable by the results which have been obtained in experiments with discharge tubes containing the halogens, metallic vapours, and other gases. It is probable that, under proper conditions, the aluminium cathode will disintegrate in gases more or less rapidly. This has, at any rate, been found to take place in presence of the halogens, cyanogen, pentane, benzene vapour, cadmium vapour, mercury dimethyl, and carbon dioxide. In the case of the halogens, the rate of disintegration increases with the molecular weight of the gas.

The disintegration appears to take place most readily when pressure in the discharge tube has reached the ordinary first stage, and when the cathode dark-space has reached the wall of the tube surrounding the cathode.

Under certain conditions disintegration seems to be due to and experiments are described which indicate that a very small amount of water-vapour may in some cases be the cause of the phenomenon. It may also be due to a thin film of oxide or nitride on the surface of the cathode, which must first be removed by bombardment by the positively charged particles. H. M. B.

The Rôle of Valency in the Additiveness of Diamagnetism.
PAUL PASCAL (*Compt. rend.*, 1914, 159, 429—431).—In organometallic compounds of the metals lead, tin, or mercury the diamagnetism of the metal in an homologous series of compounds varies from an upper limit at the lower end of the series to a lower limit at the upper end of the series. In the form of salts the atomic coefficient of magnetisation of quadrivalent lead and bivalent tin tend toward the inferior limit, of bivalent lead and quadrivalent tin toward the upper limit. Mercury, on the other hand, has the same atomic coefficient both in mercurous and mercuric salts, the value differing notably from that of pure mercury and approaching the upper limit in its series of organometallic compounds. The neighbourhood of several halogen atoms around the same central atom depresses the diamagnetism in inorganic chemistry as well as in organic chemistry, but it is impossible at present to give a rule for calculating the value of this diminution. W. G.

Specific Heats of Liquids at Various Constant Pressures and Various Temperatures. II. SILVIO LUSSANA (*Nuovo Cimento*, 1914, [vi], 7, i, 301—312. Compare A., 1912, ii, 1135). Further measurements on ethyl ether at higher temperatures than those previously employed show that, as with ethyl and amyl alcohol, the diminution of c_p as the pressure rises tends to become lower at the higher temperatures and pressures; at a sufficiently high pressure the variation of c_p changes its sign. The value of c_p also diminishes as the temperature and pressure rise. If the external work effected in liquids during heating be neglected and the difference between the two specific heats be attributed solely to the internal work, these results and the variations of the coeff.

mination at constant pressure with the pressure and temperature would show that the amount of internal work necessary during heating diminished with increase of the pressure.

The conclusion is drawn that the diminution of the distance between the molecules of liquids, which is naturally accompanied by restriction of the liberty of movement of the molecules, carries with it a diminution in the value of γ , and hence tends to cause the heat consumed during heating to aid the molecular energy.

T. H. P.

Frosting Point of Benzene as a Fixed Point in Thermometry. THEODORE W. RICHARDS and JOHN W. SUMPTER (*J. Amer. Chem. Soc.*, 1914, **36**, 1825—1832).—The most convenient and exact way of fixing points on the thermometric scale between 0° and 100° is probably by means of the transition temperatures of hydrated crystalline salts (compare A., 1898, ii, 555; 1899, ii, 354; 1903, ii, 11, 1906, ii, 727; 1908, ii, 16; 1911, ii, 695; this vol., ii, 244). The f. p. of a liquid can also be used for this purpose, and a useful study has therefore been made of the f. p. of benzene. Benzene of sufficient purity can be prepared without much difficulty, and yields a very definite and constant f. p., 5°483° ± 0.002° in conjunction with the f. p. of water, is of value for calibrating Beckmann thermometers.

E. G.

Calculation of Chemical Constants. UGO GRASSI (*Nuovo Cim.*, 34, [vi], 7, i, 313—320).—By means of measurements made on a group of fourteen compounds, Mündel (this vol., ii, 28) found that the values of the chemical constant, C , which give good agreement between the observed values of p and those determined by means of Nernst's equation, $\log p = -\lambda_0/4571T + 1.75 \log T - 4.571 + C$, differ markedly from those previously calculated by Nernst himself. The latter made use of the equation,

$$\Lambda = (\lambda_0 + 3.5T - \epsilon T^2)(1 - \rho_0 \pi_0),$$

in conjunction with that given above, but the thermochemical data at his disposal referred only to a restricted temperature interval, so the values of the constants ϵ and λ_0 were derived by a precarious approximation. The author has determined these constants more exactly from the value of π , and that of p at two temperatures differing considerably from the critical temperature and from one another.

The following latent heats of evaporation at 0° were determined, the numbers being cal. per gram (compare this vol., ii, 184): methyl ethyl ketone, 124.2; diethyl ketone, 112.85; dipropyl ketone, 87. propyl alcohol, 192.2; pinacolin, 98.53. By means of Stieglitz's method the following critical pressures were measured: propyl ketone, 33.9; diethyl ketone, 42.5; and methyl ethyl ketone, 47.5 atmos. The values of the chemical constants calculated from the two above formulae are as follows, those given by Nernst's rule being shown in brackets: acetone, 3.74 (3.02); methyl ethyl ketone, 4.50 (2.97); diethyl ketone, 4.54 (2.92);

dipropyl ketone, 5.59 (2.90); ethyl formate, 6.56 (2.92); propyl formate, 4.10 (3.14); methyl acetate, 5.73 (2.96); ethyl acetate, 5.05 (2.93); benzene, 4.37 (2.88); isopropyl alcohol, 4.94 (3.7).

T. H. P.

Trotton's Rule. CARLO SONAGLIA (*Nuovo Cim.*, 1914, **vii**, 1, 321-328). - Cederberg's objection to Nernst's equation (1911, **vii**, 854), on the ground that it contains no constants related to the particular compound, is invalid, since the boiling point enters into the equation. Cederberg claims for his own equation that it contains no empirical constants; since, however, it is derived by combining other relations with van der Waals' equation, the values of a are not the same, but different for different compounds, this claim is open to criticism.

The author has investigated the values of Trotton's constant for ethyl and propyl formates, methyl and ethyl acetates, and for methyl ethyl ketone, diethyl ketone, and dipropyl ketone at various temperatures, which exactly correspond. Use is made of Nernst's formula, $\lambda = (\lambda_0 + 3.5T - \epsilon T^2)(1 - p/\pi_0)$, in which ϵ is a constant and λ_0 the latent heat of evaporation at absolute zero. Accurate measurements of λ at two different temperatures give the values of λ_0 and ϵ , and hence the value of λ at any other temperature so long as p is small compared with the critical pressure, π_0 . At reduced temperatures equal to or greater than 0.5 this condition is not satisfied, and in these cases p was calculated by means of Nernst's formula, $\log p = \lambda_0/4.571T + 1.75 \log T - \epsilon T/4.571$.

The results show that the values of Trotton's constant for the esters become equal at a reduced temperature of about 0.5, while at lower temperatures marked variations occur. Nernst's contention, that the values at the boiling point increase with the temperature, is not confirmed for the values at corresponding temperatures.

On the other hand, the curves representing the variation of Trotton's constant with temperature for the last three ketones are similar, but do not meet; the behaviour of acetone is controlled by the tendency of its molecules to associate. T. H. P.

Rapid Laboratory Method of Measuring the Partial Vapour Pressures of Liquid Mixtures. M. A. ROSENBOFF, C. W. FOX and R. H. WHITE (*J. Amer. Chem. Soc.*, 1914, **36**, 1803-1812). - The usual method of obtaining partial pressure data by distilling off a small quantity of the liquid and determining its vapour pressure (Zawidzki, A., 1901, **ii**, 6) gives good results. A simpler and more rapid method has now been devised, which has been applied to both binary and ternary mixtures, and is recommended as the easiest means of ascertaining the composition of vapour-liquid equilibrium with liquid mixtures. Instead of allowing the distillate to accumulate in the receiver, seven or eight consecutive small fractions are removed and analysed separately. The composition and weights of these fractions being known, a curve can be constructed indicating the composition of the distillate when its weight is

gained any definite amount within the range of the curve. A moderate extrapolation backwards leads to the point at which the sum of the distillate is zero. The point of intersection indicates the decomposition of the first indefinitely small amount of vapour raised by the liquid mixture.

Apparatus is described for carrying out determinations by this method, and the results of measurements are given for mixtures of carbon disulphide and carbon tetrachloride, chloroform and acetone, acetone and toluene, and ethyl iodide and ethyl acetate. The measurements were carried out isopiastically under ordinary atmospheric pressure. The method can be employed in cases in which the amount of substance available is too small to yield accurate results by the older methods.

E. G.

Apparatus with Ground-joints for the Distillation in Vacuum of Substances Attacking Cork. HENRI VIGRUX (*See Chem. anal.*, 1914, **19**, 220–221).—A glass apparatus consisting of distilling flask, fractionating column, and receiver, in which joints are ground, is figured and described; it may be used for distillation under ordinary or reduced pressure. A glass tube supporting the thermometer is ground into the top of the fractionating column, and contains mercury, to secure rapid equalisation of temperature.

C. S.

Thermoelement Installations, Especially for Calorimetry. WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1914, **36**, 1856–1868).—The greatest precision in calorimetric work is obtainable by the use of electrical thermometers. The most satisfactory of these, and the most accurate for small intervals, is the multiple thermoelement, when used with a small difference between its two ends. An account is given of the methods and apparatus employed in the electric procedure, and a type of auxiliary installation for measurements is described which is convenient, rapid, and capable of the high precision often required for calorimetry. A precision of 1 microvolt can be obtained with the use of a suitable rotating switch and an appropriate potentiometer. For the latter, a common copper knife switch is serviceable. Satisfactory potentiometers are described in a separate paper (following article).

E. G.

Potentiometers for Thermoelectric Measurements, Especially in Calorimetry. WALTER P. WHITE (*J. Amer. Chem. Soc.*, **36**, 1868–1885). Potentiometers are described which are peculiarly adapted for high-temperature measurements in cases where the sensitiveness and precision of the thermoelement is in excess of the requirements. Split circuit and combination potentiometers are satisfactory and easily obtainable, but the Wagner and Feussner potentiometers of a range of 1 volt or more are not suitable for thermoelement work. The potentiometer can be conveniently used for simultaneous measurements of different temperatures by varying *E.M.F.*'s, and also enables the last two

figures of any reading to be taken directly from the galvanometer scale. It increases speed, simplifies manipulation, diminishes errors, and gives calorimetric data in a convenient form for further treatment.

E. G.

Surface Tensions of Liquids in Contact with Different Gases. ALLAN FERGUSON (*Phil. Mag.*, 1914, [vi], **28**, 403-412).—From observations of the maximum pressure required to remove a bubble of gas from the end of a vertical capillary tube immersed in the liquid, the author has determined the surface tension of benzene, chloroform, water, methyl alcohol, ethyl alcohol, ether, and turpentine in contact with (1) air, (2) carbon dioxide. In all cases, the liquid was found to have a smaller surface tension in contact with carbon dioxide; the largest difference, amounting to 2.05%, is shown by chloroform, and the smallest difference, 0.46%, by turpentine.

The observed effect is not only influenced by the nature of the gas, but also by its solubility in the liquid. Since the gas is however, only sparingly soluble in the liquids examined, it is probable that the values obtained differ only very slightly from the values for gas-free liquids.

H. M. H.

Absorption of Dextrose by Bone-black. HAROLD A. MARSH (*J. Amer. Chem. Soc.*, 1914, **36**, 1832-1838).—In the course of certain work on the sugars, it was necessary to purify a large quantity of dextrose. During this purification it was observed that a considerable amount of the dextrose was removed by bone-black from the aqueous solution. In order to investigate this phenomenon, solutions of dextrose of concentrations from 10% to 50.58% were treated with purified bone-black, and afterwards examined polarimetrically. The results show a regularity indicating that the absorption of dextrose by bone-black follows a principle resembling the distribution law. The ratios of the weight of dextrose per gram of solution to that per gram of bone-black are almost identical for all the concentrations. The data obtained in these experiments show that the bone-black takes part of the water from the solutions as well as the dextrose, and that the absorption of the water takes place according to some process similar to that followed in the absorption of dextrose. When equilibrium has been attained, the solution of dextrose without bone black is at least twice as concentrated as the solution containing

F. G.

Morphological Studies of Benzene Derivatives. VII. The Correlation of the Forms of Crystals with their Molecular Structure and Orientation in a Magnetic Field in the Case of Hydrated Sulphonates of Dyad Metals. H. E. STRONG and E. H. RUM (Proc. Roy. Soc., 1914, [A], **90**, 463-472).—Compare this vol. i, 1062; ii, 413).—The work recorded in this paper has particular reference to the behaviour of crystals, especially of salts of the magnetic and other dyad metals, when ex-

posed in a strong magnetic field. Salts of these metals with benzene-sulphonic, toluene-*p*-sulphonic, *p*-chloro-, *p*-bromo-, *p*-iodo, and *p*-dichloro-benzenesulphonic acids have been prepared, and the following new crystallographic data are given. All the salts crystallise in the monoclinic system, the last two in the hemimorphic class.

	$a : b : c$	δ
$(C_6H_5SO_3)_2Fe \cdot 6H_2O$	3.5690 : 1 : 1.1038	86.18°
$(C_6H_5SO_3)_2Co \cdot 6H_2O$	3.5560 : 1 : 1.1036	86.7°
$(C_6H_5SO_3)_2Ni \cdot 6H_2O$	3.5470 : 1 : 1.1076	86.9°
$(C_6H_5MeSO_3)_2Fe \cdot 6H_2O$	3.5972 : 1 : 1.1031	88.3°
$(C_6H_5MeSO_3)_2Co \cdot 6H_2O$	3.5903 : 1 : 1.1080	88.17°
$(C_6H_5MeSO_3)_2Ni \cdot 6H_2O$	3.5949 : 1 : 1.1039	88.31°
$(C_6H_5ClSO_3)_2Fe \cdot 6H_2O$	3.6781 : 1 : 0.9094	94.21°
$(C_6H_5ClSO_3)_2Co \cdot 6H_2O$	3.6608 : 1 : 0.9071	93.46°
$(C_6H_5BrSO_3)_2Fe \cdot 6H_2O$	3.7293 : 1 : 0.9104	94.26°
$(C_6H_5BrSO_3)_2Co \cdot 6H_2O$	3.7103 : 1 : 0.9087	93.59°
$(C_6H_5BrSO_3)_2Ni \cdot 6H_2O$	3.7316 : 1 : 0.9139	94.34°
$(C_6H_5I_2SO_3)_2Fe \cdot 6H_2O$	3.7856 : 1 : 0.9055	93.35°
$(C_6H_5I_2SO_3)_2Co \cdot 6H_2O$	3.7543 : 1 : 2.1053	78.40°
$(C_6H_5Cl_2SO_3)_2Co \cdot 6H_2O$	3.7456 : 1 : 2.1034	78.15°

The benzenesulphonates, toluenesulphonates, and *p*-halogenbenzenesulphonates form three distinct isomorphous series, between each of which, however, there is a close morphotropic relationship; the salts of the dichloro-series, however, show no obvious connexion with those of the other three. When the salts of any one metal (the first three series are considered), their crystals are found to respond in magnetic behaviour as they do in geometrical structure; that is to say, corresponding directions set in the same manner in the magnetic field. The salts of different metals, however, differ greatly in magnetic behaviour. In the case of all the iron salts, the c -axis is the direction of greatest magnetic permeability, whilst in the cobalt salts this direction is that of least permeability. The *p*-iodo salts differ from both those of iron and cobalt, but appear to be similar to those of copper, manganese, and magnesium. Similar differences are found between the sulphates of the magnetic metals and between the double salts which those form with ammonium sulphate. The relation between the molecular and crystalline structure of the sulphonates is discussed from the *W. Pope* point of view, and also the use which may be made of the magnetic property of crystals for determining the correct setting.

In an appendix, data are given for the crystalline form of tescum *p*-chlorobenzenesulphenate, which is found to be in close morphotropic relationship with the corresponding iron and cobalt salts. The salt, which is anhydrous, crystallises in the monoclinic system, $a : b : c = 1.4394 : 1 : 0.9049$; $B = 97.11^\circ$. The behaviour of benzene in the magnetic field is also considered in the light of the suggestion that there may be some connexion between magnetic susceptibility and the colour of the crystals. E. H. R.

Growth of Metallic Eutectics. E. E. E. LAMPLAUGH and J. T. MOTT (*Proc. Roy. Soc.*, 1914, [A], 90, 600—604).—The influence of

undercooling on the structure of certain binary alloys has been examined. It has been supposed that the formation, around the primary crystals of an alloy, of an envelope of the second constituent separating the primary crystals from the banded structure, is due to undercooling in the process of solidification. The experiments which have been made by the authors indicate that this is not the case, and there appears to be no connexion whatever between the undercooling at the first moment of solidification and the formation of such a halo or envelope.

From the examination of a large number of alloys, it has been found possible to classify eutectics according to their structure. The majority of eutectics fall into two classes, which are characterised, respectively, (1) by spherical radiating growths, and (2) by well-defined crystal contours, showing in section a herringbone structure.

H. M. P.

Hermannus Follinus and the Law of the Indestructibility of the Elements. W. P. JORISSEN (*Chem. Weekblad*, 1914, 11, 822-826).—In 1613, Follinus observed that a given weight of mercury could be transformed into mercuric sulphide, and that the product could be oxidised to mercury without change in the weight of the metal.

A. J. W.

History of Condensers. MAX SPETER (*Chem. Zentral*, 1914, 19, 1798; from *Chem. Apparal*, 1914, 1, 65-70).—A critical discussion regarding the history of condensers. The author suggests that the Liebig condenser should be known by the name of its inventor Weigel.

W. P. S.

Simple Method of Making Dewar's Tubes. HENRI VIGER (*Ann. Chim. anal.*, 1914, 19, 293-294).—A glass tube of small diameter is drawn out to a fine tube at one end, whilst the other end is rounded, like the bottom of a test-tube. This end is heated, the end is drawn in so as to form a concave cap, and while the end of the tube is kept in the flame, an iron rod is pressed into the cup so as to force it into the outer tube to a sufficient depth. The tube is then silvered and exhausted.

W. P. S.

Device to Aid in Freeing a Precipitate from Mother-liquor when Filtering by Suction. Ross AIREY GOETZNER (*Amer. Chem. Soc., 1914, 36*, 1967).—When a precipitate has been collected and drained in a Buchner funnel, a further quantity of the mother-liquor can be removed from it by placing a piece of thin sheet rubber over the top of the funnel and securing it by means of a rubber band. The suction draws the rubber over the sides of the funnel and on to the top of the precipitate. The surface of the rubber may now be firmly pressed off by hand or with a pestle, and in this way the precipitate can be obtained in a comparatively dry condition.

E. G.

Inorganic Chemistry.

Reduction of Chlorates to Chlorides by Hydrazine Salts with the Aid of a Catalytic Substance. W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1914, **33**, 815).—Solutions of alkali or other chlorates (bromates or iodates) and hydrazine salts may be mixed together in any proportion and boiled without any reaction taking place. If, however, a piece of tarnished copper wire or a fragment of copper oxide is introduced into a cold solution of potassium chlorate and hydrazine nitrate, an action commences at the surface which is rapid, nitrogen being evolved. The reaction is accelerated by warming, and is quantitative, in accordance with the following equation. $2\text{KClO}_3 + 3\text{N}_2\text{H}_4 \cdot \text{HNO}_3 = 6\text{H}_2\text{O} + 3\text{N}_2 + 3\text{HNO}_3 + 2\text{KCl}$. The amount of copper dissolved is very small; various copper salts produce a like result. When used for the estimation of chlorates, bromates, or iodates, the slight excess of hydrazine salt used is destroyed by permanganate mixed with nitric acid; the chloride, bromide, or iodide present in the solution is then estimated.

Hydrazine sulphate and oxalate do not react so well as the perchlorate with copper and its salts; in the presence of metallic iron or iron salts the reaction with the sulphate is violent, whereas it is very slow with the nitrate and oxalate.

Reference is also made to the action of hydrazine salts on di-nitroates, arsenates, persulphates, osmates, molybdates, tungstates, manganates. Perchlorates are not reduced in the same way as chlorates; ammonium perchlorate and hydrazine nitrate may be melted together without decomposition. T. S. P.

Existence of Free Thiosulphuric Acid. C. BONGIOVANNI (*Borsone*, 1914, **44**, i, 624–627).—When an aqueous alcoholic solution of methylene-blue is added to an acidified solution of a thiosulphate, it is decolorised. Sulphurenic acid does not effect this reaction, which is an indication of the presence of free thiosulphuric acid in the solution. R. V. S.

The Crystal Form of Some of the Hydrated Haloid Salts of the Alkali Metals. C. W. COOK (*Amer. J. Sci.*, 1914, [iv], **38**, 6, 114).—The majority of these hydrated haloids effloresce easily at the ordinary temperature, in consequence of which the crystallographic data recorded are incomplete, and of only approximate accuracy. The salts were not analysed, the formulae being based on that given by Mitscherlich for the sodium bromide.
 $\text{KF}_2\text{H}_2\text{O}_3$; monoclinic prismatic; $a : b : c = 1:0565 : 1:070608$; $\gamma = 109^\circ 15'$.
 $\text{RbF}_2\text{H}_2\text{O}_3$; monoclinic prismatic; $a : b : c = 0:83665 : 1:11188$; $\gamma = 104^\circ 15'$.
 $\text{NaBr}_2\text{H}_2\text{O}$; the constants for this salt could not be determined. The value of the angle (110): (110) is $61^\circ 24'$. E. H. R.

Isomorphism between Perchlorates and Permanganates. G. SCAGLIARINI and A. MARANGONI (*Atti R. Accad. Lincei*, 1914, **v**, *23*, ii, 12-14).—The action of sodium perchlorate on a concentrated ammoniacal solution of silver nitrate yields the compound $\text{AgClO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$, which forms acicular crystals sensitive to the influence of light. The analogous compound, $\text{AgMnO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ (compare Klobb, A., 1886, 983), forms dark, acicular crystals with metallic lustre. These two salts form mixed crystals, which may contain up to about 25% of the permanganate compound.

The compounds $\text{Mg}(\text{MnO}_4)_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 8\text{H}_2\text{O}$ and
 $\text{Ni}(\text{MnO}_4)_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 8\text{H}_2\text{O}$

have also been prepared by the action of hexamethylenetetramine on magnesium and nickel permanganates. T. H. P.

Synthetic Celite and Large Crystals of Tricalcium Silicate. EDWARD D. CAMPBELL (*J. Ind. Eng. Chem.*, 1914, **6**, 705-710).—Celite consists essentially of a calcium aluminate, m.p. slightly above 1400° ; it has the formula $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, and is capable of dissolving, when liquid, calcium orthosilicate and calcium oxide. If the concentration of the calcium oxide is sufficient and soln. is complete, pure tricalcium silicate crystallises out when the mass is cooled slowly. This suggests a new theoretical formula for Portland cement. The Le Chatelier formula first proposed is $x(3\text{CaO} \cdot \text{SiO}_3) + y(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$, requiring calcium oxide by weight equal to $2.8\text{SiO}_2 + 1.6\text{Al}_2\text{O}_3$; in practice this gives a large excess of free calcium oxide. In the Newberry formula,
 $x(3\text{CaO} \cdot \text{SiO}_3) + y(2\text{CaO} \cdot \text{Al}_2\text{O}_3)$,

the calcium oxide is equivalent to $2.8\text{SiO}_2 + 1.1\text{Al}_2\text{O}_3$, and this gives an excess of free lime in the cement. The formula suggested would be $x(3\text{CaO} \cdot \text{SiO}_3) + y(5\text{CaO} \cdot 3\text{Al}_2\text{O}_3)$, where the calcium oxide by weight would be equal to $2.8\text{SiO}_2 + 0.9\text{Al}_2\text{O}_3$. Such a formula would conform more closely with the results obtained in the best practice. W. P. S.

The Dissolution Faces of Dolomite. P. GAUBERT (*Congr. rend.*, 1914, **159**, 486-488).—When a cleavage rhombohedron of dolomite is attacked by boiling nitric acid, scalenohedral facets appear. The positions of these facets can be determined, and are found to vary in a regular manner with the rate of attack of the acid on the crystal, the indices ranging from $(11,1,0)$ to $(410,1,1)$. In the same manner, the form of the corrosion figures on different faces of the crystal varies with the rate of attack. Specimens of dolomite are attacked more slowly by acid of a given concentration the more iron they contain, and the position of the dissolution facets varies accordingly. E. H. E.

The Ternary System. Diopside-Forsterite-Silica. N. J. BOWEN (*Amer. J. Sci.*, 1914, [iv], **38**, 207-264).—An account is given of the equilibrium relationships in the ternary system $\text{CaMg}(\text{SiO}_4)_2 \cdot \text{Mg}(\text{SiO}_4) \cdot \text{SiO}_2$, which represents that part of the more general ternary system $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$, which is of greatest interest to the petrologist.

The method of experiment consisted in heating mixtures of specially purified silica, magnesia, and calcium carbonate at known temperatures in an electrical resistance furnace until equilibrium was attained, when the mixtures were rapidly cooled, and afterwards examined under the microscope.

The binary system Mg_2SiO_4 - SiO_2 has been described in a previous paper (Bowen and Andersen, this vol., ii, 562). The system $CaMg(SiO_3)_2$ - SiO_2 shows the simple eutectic relation. Diopside melts at 1391° , and the eutectic temperature 1362° , at which diopside and tridymite co-exist, corresponds with the composition 84% diopside and 16% silica. A break on the silica quadrilateral is shown at 1470° , and this in all probability corresponds with the transformation of tridymite into cristobalite. The system $CaMg(SiO_3)_2$ - Mg_2SiO_4 also shows the eutectic relation. The eutectic point, at the composition 88% diopside and 12% forsterite, is only 4° to 5° lower than the melting point of diopside.

The above three binary systems give rise to five solid phases—diopside, cristobalite, tridymite, clino-enstatite, and forsterite. In the normal ternary equilibrium diagram there would be five corresponding surfaces, six boundary curves, and three ternary invariant points. The experimental results indicate, however, that diopside and clino-enstatite form an unbroken series of solid solutions (enstatitic pyroxenes), with the result that diopside, clino-enstatite, and the intermediate pyroxenes have but one surface in common. There are, consequently, only three boundary curves and one ternary point, namely, that corresponding with the co-existence of cristobalite, tridymite, and pyroxene.

The optical properties of the various crystalline phases have been examined, and it has been found that the properties of the pyroxenes vary continuously with the composition. In considering the bearing of the results on petrologic problems, attention is called to the resorption of forsterite in the artificial mixtures and its probable connexion with the resorption of olivine in natural rocks.

H. M. D.

Oxy-haloiods of Lead. G. SANDONNINI (*Atti R. Accad. Lincei*, 34, v, 23, i, 959-965).—Thermal and micrographic study of the system PbO - $PbBr_2$ confirms the existence of the compound $PbBr_2PbO$ at high temperatures, and of $PbBr_2.2PbO$, and indicates also the existence of the compound $PbBr_2.4PbO$, which decomposes on melting. No formation of solid solutions between the various oxybromides is observed.

The system PbO - PbF_2 does not form a compound, but a simple eutectic, m. p. 494° , containing about 54 mol. % of PbO , is observed.

T. H. P.

Arsenates of Lead. HERMAN V. TARTAR and R. H. ROBINSON (*J. Amer. Chem. Soc.*, 1914, 36, 1843-1853).—The extensive use of lead arsenates as insecticides has rendered a knowledge of their constitution and properties of considerable importance, and the present investigation was therefore undertaken.

Lead hydrogen arsenate can be obtained in a fairly pure condition by the following method. The precipitate produced by the interaction of lead nitrate and disodium hydrogen arsenite is washed with water and dissolved in just sufficient nitric acid to effect solution. Dilute ammonia is added gradually to the solution until about three-fourths of the nitric acid has been neutralised. The precipitate of lead hydrogen arsenate so obtained is left in contact with the solution for some hours and is then collected, washed with freshly boiled water, and dried at 110°. The product contains a small quantity of water, which is not expelled below 200°. When heated somewhat above 200° it is converted into lead pyroarsenate.

Attempts to prepare lead orthoarsenate by the action of ammonium hydroxide on lead hydrogen arsenate, as suggested by Volck (*Science*, 1911, **33**, 868), resulted in the formation of a basic compound, $21\text{Pb}_3(\text{AsO}_4)_2 \cdot 2\text{Pb}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$, as an amorphous powder. Pure lead orthoarsenate could not be obtained.

Lead hydrogen arsenate has $D_4^{\infty} 5.786$, and basic lead arsenate $D_4^{\infty} 7.105$. Both compounds are very little, if at all, soluble in water.

The precipitates obtained by the reactions of lead acetate and lead nitrate with disodium hydrogen arsenite are not free from lead hydrogen arsenate and the basic lead arsenate in proportion varying with the conditions of the experiments. E. C.

Atomic Weight of Copper by Electrolysis. A. M. S. SUMMERTON (*Proc. physical Soc. London*, 1914, **26**, 29^a; 312). The relative quantities of copper and silver deposited by the same current have been determined in order to obtain the atomic weight of copper.

For the production of an uniform coherent deposit of pure copper it was found necessary to maintain the current density at the cathode below a certain limiting value. This limiting value was determined in a series of preliminary experiments, and found to depend on the form of the electrolytic cell, the concentration of the electrolyte, the presence of acid and other impurities, the presence or absence of a porous pot, and in the case of a rotating cathode on the speed of rotation. In order to prevent the formation of loose crystalline clusters, it was also found necessary to regulate the current density according to the weight of the metal to be deposited. Empirical formulae are given from which the limiting current density can be calculated.

In the actual experiments four copper cells, placed between two silver cells, were run in series. The surfaces of the copper cathodes varied from 10 to 50 cm.², and the actual weights of the deposits were plotted against the corresponding cathode surface in order to eliminate the effect of cathodic dissolution by extrapolation to zero cathode surface. Ten values obtained in this manner give for the atomic weight of copper 63.563 ± 0.003 , the silver is taken as 107.88. H. M. D.

The Crystalline Structure of Copper. W. LAWRENCE BRAGG (*Proc. Roy. Soc., Mag.*, 1914, [vi], **28**, 353—360).—The author has applied the X-ray method of investigation to the study of natural crystals of copper. The surfaces of these crystals reflect the rays satisfactorily after being etched with nitric acid, and although the faces are considerably distorted, a good standard of accuracy is obtainable with the X-ray spectrometer. The results show that in a copper crystal the atoms are arranged on a face-centred cubic lattice, identical with the close-packed lattice suggested by Barlow and Bernal for elementary substances.

E. H. R.

Mineralogical Chemistry.

Octahedral Crystals of Sulphohalite. HOYT S. GALE and W. R. HINES (*Amer. J. Sci.*, 1914, [iv], **38**, 273—274).—Octahedral crystals, obtained from drillings in the saline deposits at Searles Lake, California, gave on analysis numbers which agree with those represented by the formula for sulphohalite, $2\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot \text{NaF}$. Measurements of the density and refractive index gave $D = 2.5$ and $n = 1.455$.

H. M. D.

Analytical Chemistry.

Some Natural Indicators. H. W. BRUBAKER (*J. Amer. Chem. Soc.*, 1914, **36**, 1925—1928).—An account is given of the behaviour of colouring matters of the petals of various flowers towards bases and acids. These substances are usually acid, but some are neutral in character, and generally change colour in acids or alkalies, thus acting as indicators. Many of the colouring matters are very sensitive to the action of light and air.

E. G.

Electro volumetric Method and its Application to General Analytical Chemistry. F. H. HESSELINK VAN SCHUTEN and K. DE ITIANO (*J. Amer. Chem. Soc.*, 1914, **36**, 1793—1803).—The difficulties encountered in the use of indicators in volumetric analysis, such as the personal equation and the interference of the colour of the liquid with that of the indicator, have led the authors to study the conductivity method of estimation (compare Ester, Grüters and Geibel, A., 1905, ii, 55; Hall and Bell, A., 1911, ii, 637). This method has been applied to the estimation of acids, bases, salts, and mixtures of salts, and has been found very satisfactory. Curves have been constructed by plotting the conductivities as ordinates and number of c.c. of the reagent as

absence. The method is also of service for the estimating of chlorine and phosphates in urine. E. G.

Apparatus for the Analysis of Mixed Gases. A. C. WILKS (*Analyst*, 1914, **39**, 391-392).—A modification of Stead's apparatus is described. Mercury is used as the confining medium, and the absorption bottles are each provided with a side-tube, to which is attached a thin gas-bag. Combustion of the gas mixture is effected in a graduated eudiometer tube fitted with platinum terminals, or a palladium tube may be employed. W. P. S.

Apparatus for Exact Gas Analysis. E. MAGUIN (*J. de Chim. anal.*, 1914, **19**, 298-300).—A measuring burette is connected by means of a three-way tap with a gas vessel and an absorption pipette, which is provided at the top and bottom with three-way taps. The burette is also in connexion with a levelling tube. The apparatus and the capillaries between the pipette and the burette are filled with mercury, and, when the gas has been introduced into the burette and driven over into the pipette, the absorption solution is admitted to the latter. When absorption has taken place, the solution is withdrawn from the pipette by connecting the latter with an exhaust pump, and the gas is then passed again into the burette. W. P. S.

Absorption Vessel for Gas Analysis. E. MAGUIN (*Ann. Gas anal.*, 1914, **19**, 219-220).—A modified form of absorption vessel for the Orsat apparatus, in which intimate contact with the absorbing liquid is obtained, the gas on entering the vessel being caused to pass through the liquid in very small bubbles, and the remaining in contact with broken glass moistened with the absorbent. Two automatic valves cause the gas to pass in the required directions when entering or leaving the vessel. L. DE K.

Estimation of Iodine and Bromine in Halogen Salts by Means of Telluric Acid. HARRIET ISABELLE COLE (*Amer. J. Sci.* 1914, [iv], **38**, 265-272. Compare this vol., ii, 379).—Quantities of iodine or bromine up to 0.3 gram when associated in the halogen salts with 0.25 gram of chlorine may be estimated as follows. Weighed amounts of the three salts, for instance, 0.1 gram each of iodide, bromide, and chloride, are introduced into a graduated tubular flask and dissolved in 50 c.c. of water. The flask is connected with a receiver containing 200 c.c. of 1 per cent potassium iodide solution, and cooled in ice-water. After the addition of 1 gram of telluric acid, dissolved in 15 c.c. of sulphuric acid (D 1.015) and 35 c.c. of water, the solution in the flask is heated to boiling, and a current of carbon dioxide is passed through it until all the liberated iodine has been distilled, the volume of the solution being kept at 100 c.c. The steam is then diminished, and the solution concentrated to 65 c.c. The iodine in the distillate is now titrated with thiosulphate solution.

The receiver is recharged with potassium iodide solution, and, after the addition of 10 c.c. of sulphuric acid (1:1) to the contents of the smaller flask, the distillation with steam and carbon dioxide is continued, the volume being kept constant until all bromine evolution has been expelled; the solution is then concentrated slowly to 30 c.c., next rapidly to 24 c.c., and the distillate is titrated with thiosulphate solution; the iodine thus titrated is equivalent to the quantity of bromine distilled. W. P. S.

Volumetric Method of Estimating Sulphurous Acid. CHARLES S. JAMIESON (*Amer. J. Sci.*, 1914, [iv], 38, 166-168). - The method is based on the titration of sulphurous acid with potassium iodate solution in the presence of 15 to 20% of hydrochloric acid and a small quantity of an immiscible solvent, such as chloroform. The sulphurous acid solution is added to a cooled mixture of 30 c.c. of concentrated hydrochloric acid, 20 c.c. of water, and 6 c.c. of chloroform, and the solution is then titrated with standardised potassium iodate solution. The latter is at first run in rapidly until the iodine which is liberated reaches a maximum, and then soon disappears. The mixture is now shaken thoroughly, and titration continued, the end-point being denoted by the disappearance of the violet colour from the chloroform. When dealing with quantities of sulphurous acid or sulphite equivalent to less than 0.1 gram of sulphur dioxide, it is advisable to add 5 c.c. of monochloride solution to the hydrochloric acid mixture before the sulphurous acid is introduced; this prevents loss of sulphur dioxide before the titration is carried out. W. P. S.

A Simplification of the Estimation of Total Nitrogen by Colorimetry. ADDISOS GULICK (*J. Biol. Chem.*, 1914, 18, 541-547). - An improvement on the Folin-Farmer colorimetric method for estimating total nitrogen in urine (A., 1912, ii, 702) is described by the author which avoids the necessity of separating the urine by aspiration from the products of oxidation. This is effected by oxidising the urine with a very small quantity of nitric acid in the presence of potassium sulphate and mercuric nitrate, so that the subsequent colour reaction with a modified Folin's reagent is not interfered with. The resulting method is found to be expeditious and accurate, and requires less apparatus than the microchemical methods now employed. H. W. B.

Reduction of Disodium Phosphate by the Alternating Current. P. WENGER and L. HEINEN (*Ann. Chim. anal.*, 1914, 19, 157-171). - Tables (compare A., 1912, ii, 624, 1038) are given showing the effect on the reduction of disodium phosphate of the alternating current under various conditions, such as the period of the experiment, the concentration of the liquid, the number of electrodes, the periodicity of the current, and the temperature. The phosphites formed during the experiments are estimated very satisfactorily by means of Rupp and Finck's process (with standard phosphate in the presence of sodium hydrogen carbonate).

L. DE K.

Hypothetical Combinations in Water Analysis. R. B. BOYD (*J. Ind. Eng. Chem.*, 1914, **6**, 710—714).—In view of an effort which is being made by committees of the American Chemical Society, the American Public Health Association, and the Association of Agricultural Chemists to agree on a uniform manner of reporting results of water analyses, the author discusses the present methods of expressing results of analyses, and draws attention to the advantages of reporting the constituents in ionic form.

W. P. S.

Estimation of Silver and Base Metal in Precious Metal Bullion. FREDERIC P. DREWRY (*J. Ind. Eng. Chem.*, 1914, **6**, 650—658, 728—736).—The cadmium-thiocyanate method (fusion of the metal with lead and cadmium in potassium cyanide, ignition of the button in nitric acid, and titration of the silver in thiocyanate solution) for the estimation of silver in gold was found to be quite as trustworthy as the ordinary cupellation method.

W. P. S.

Separation and Estimation of Small Quantities of Lead in Solders, Tinfoil, etc. PIERRE BRETEAU and PAUL FIRMIER (*J. Pharm. Chim.*, 1914, [vii], **10**, 147—152).—The authors point out sources of error when, after dissolving the alloy in nitric acid, the lead is separated by precipitation as sulphide, sulphate, or chromate, or estimated electrolytically or colorimetrically, and give in a subsequent paper details of a method for the accurate estimation of small quantities of lead in these alloys.

W. P. S.

Detection of Lead in Bismuth Subnitrate. G. GATE (*J. Pharm. Chim.*, 1914, [vii], **10**, 22—23).—In a previous communication (A., 1913, ii, 1076) a test has been described which depends on the insolubility of bismuth subnitrate in 5% ammonium nitrate solution, whilst lead sulphate, carbonate, etc., are soluble. The author now finds that certain specimens of heavy bismuth subnitrate, which are free from lead, but possibly incompletely washed, are partly soluble in boiling ammonium nitrate solution, whilst the filtered solution gives a yellow precipitate of bismuth oxide after addition of potassium chromate. It is therefore necessary to test the precipitate by adding sodium hydroxide in slight excess. If it consists solely of lead chromate, a clear solution is obtained from which reprecipitation occurs after addition of a slight excess of acetic acid; the mixed precipitate of lead and bismuth chromates, on the other hand, is only partly dissolved by the excess of acetic acid, and the filtrate then yields lead chromate after acidification. H. W.

Estimation of Mercuric Iodide in Tablets. A. W. HILL (*J. Ind. Eng. Chem.*, 1914, **6**, 753—754).—A quantity of the pure tablets, equivalent to about 0·15 gram of mercuric iodide, is heated under a reflux apparatus with 20 c.c. of hydrochloric acid and 0·5 gram of potassium chlorate until all the iodide is

J.

The solution is then cooled, diluted with water to 100 c.c., freed from chlorine by means of a current of air, and filtered. The filtrate is rendered ammoniacal, the mercury precipitated immediately with hydrogen sulphide, and the mercury sulphide is collected, dried at 100°, and weighed. The weight of the precipitate is multiplied by 1.995 to give mercuric iodide.

W. P. S.

Volumetric Estimation of Titanium by means of Ferric Chloride. T. R. BALL and G. McP. SMITH (*J. Amer. Chem. Soc.*, vol. 36, 1888—1843).—Knecht and Hibbert (A., 1903, ii, 509) have described a method for the volumetric estimation of ferric salts by means of titanium trichloride, potassium thiocyanate being used as an indicator. It is now shown that the same reaction can be employed for estimating titanium.

The solution of the titanium salt is reduced with zinc in presence of dilute sulphuric acid, and filtered; potassium thiocyanate is then added, and the solution titrated rapidly with standard ferric chloride solution. The reduction is allowed to proceed for about two hours. In order to protect the resulting titanous salt solution from oxidation, the filtration and titration are carried out in an atmosphere of carbon dioxide. A special form of apparatus for carrying the reduction and filtration is described. The method gives trustworthy results, and is much more rapid than Gooch's gravimetric method. Such metals, however, as tin, chromium, platinum, tungsten, and molybdenum must be absent when the solution is reduced.

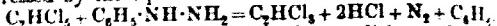
E. G.

Separation of Zirconium from Iron and Aluminium with the Aid of the Ammonium Salt of Nitrosophenylhydroxylamine ("Cupferron"). WILLIAM M. THORNTON, jun., and E. M. HODGES, jun. (*Amer. J. Sci.*, 1914, [iv], 38, 137—141). Compare this vol., p. 583.—One hundred c.c. of a solution containing zirconium, iron, and aluminium salts are neutralised with ammonia, 2 c.c. of concentrated sulphuric acid (1:1) are added, and the iron is reduced with hydrogen sulphide. The solution is then rendered slightly ammoniacal, and treated with hydrogen sulphide until all the iron has been precipitated as sulphide. This is collected on a filter and washed thoroughly with dilute ammonium sulphide solution. The filtrate is boiled to expel hydrogen sulphide, acidified with 60 c.c. dilute sulphuric acid, cooled in ice-water, and the "cupferron" reagent is added. The precipitate which forms is collected on a filter, washed twenty times with dilute hydrochloric acid, dried at 100°, ignited, and the residue of zirconium oxide weighed. In the case of phosphatic minerals, the phosphoric acid must be removed by fusion with sodium carbonate before the zirconium is separated as described.

W. P. S.

Properties of Some Chlorohydrocarbons and their Uses in Chemical Analysis. II. Estimation of the Chloroethanes. GOWING-SMITH (*Analyst*, 1914, 39, 385—388). Compare this vol., p. 101.—When tetra-, penta-, or hexa-chloroethane is treated with

phenylhydrazine, a precipitate of phenylhydrazine hydrochloride is formed, together with nitrogen and benzene. The reaction may be expressed by the equation



The reaction, however, varies with the conditions of the experiment, and the estimation of any one of the substances formed does not give a measure of the chloro-hydrocarbon. Further experiments showed that tetrachloroethane or pentachloroethane can be estimated in the following way, even in the presence of other ethylenes, chloroform, or carbon tetrachloride. Ten c.c. of a alcoholic *N*/10 potassium hydroxide solution and 20 c.c. of benzene are placed in a stoppered flask and weighed; a few drops of the chlorohydrocarbon are then introduced, and the flask is reweighed. After a few minutes water is added, the solution acidified with nitric acid, and the chloride is estimated by titration with silver nitrate and thiocyanate. One c.c. of *N*/10 silver nitrate solution is equivalent to 0.0168 gram of tetrachloroethane or 0.0202 gram of pentachloroethane. The amount of hexachloroethane in tetrachloroethane and pentachloroethane may be estimated by the method. When hexachloroethane is boiled with xylene and alcoholic potassium hydroxide solution, a deep blue coloration is produced. This reaction may afford a means for a colorimetric estimation of hexachloroethane, since the color is not given by other chlorohydrocarbons.

W. P. S.

Detection of Methyl Alcohol in Spirits. R. Vivien (*Pharm. Chim.*, 1914, [vii], 10, 145—147).—The method depends on the formation of hydrogen cyanide when methyl alcohol, or derivative, is treated with potassium hydroxide and hydroxylamine hydrochloride; ethyl alcohol, acetaldehyde, acetal, and amyl alcohol do not yield hydrogen cyanide. One hundred c.c. of the spirit to be tested are distilled, and the first 30 c.c. of distillate are treated for seven hours under a reflux apparatus with 15 grams of potassium hydroxide and 1 gram of hydroxylamine hydrochloride. The mixture is then cooled, acidified with sulphuric acid, and distilled with steam. The distillate is tested for hydrocyanic acid by the Prussian-blue test.

W. P. S.

Estimation of Alcohol in the Tropics. K. C. Brownning and C. T. Symons (*J. Soc. Chem. Ind.*, 1914, 33, 819—821).—Systematic investigations on the estimation of alcohol in the Tropics have led the authors to the conclusion that the brass Sikes's hydrometer, using the tables supplied by the makers of the instrument, gives quite inaccurate results, especially at low strengths; at no strength are the tables even approximately satisfactory. Bedford's tables, used with glass hydrometers, give the most satisfactory results except at low strengths. The brass hydrometer, used with Bedford's tables, gives very fair results.

The authors consider that the standard tables published in 1914 by the United States Bureau of Standards are the most accurate, and all alcoholic work should be based on these.

A table is given showing the relation between the refractive index at 30° and the percentage of alcohol for various mixtures of alcohol and water. The refractive index reaches a maximum at about 75.25% by weight of alcohol (compare Holmes, T., 1913, 103, 163).

T. S. P.

Verification of the Methods of Analysis of Glycerophosphates and their Preparations. M. FRANÇOIS and E. BOISMONT (*J. Pharm. Chim.*, 1914, [vii], 10, 5—14, 51—57).—The methods used in the analysis of glycerophosphates are discussed, and a scheme given for the investigation of pure and granulated calcium pyrophosphate, of the sodium salt, and also of commercial products.

Calcium glycerophosphate should be completely soluble in cold water (1 gram in 100 grams), and the solution should be neutral or slightly alkaline to phenolphthalein. It should not give a precipitate with silver nitrate (mineral phosphates), neither should it be darkened by pure sulphuric acid (various organic extractants). It should not yield a residue after extraction with 95% alcohol and evaporation of the solvent (glycerol, citric acid). Water is determined by desiccation at 150°. The residue left after calcination (pyrophosphate) is estimated by ignition in a muffle, the last traces of carbon being oxidised, if necessary, by nitroso. Phosphorus is estimated by fusing the salt with eight times its weight of potassium nitrate in a nickel dish, dissolving in cold fusion in water, precipitating the phosphoric acid with ammonium molybdate, and converting the latter precipitate into magnesium pyrophosphate. Calcium is precipitated as the oxalate in a solution of the salt which has been acidified with dilute sulphuric acid; the precipitate is ignited and weighed as calcium oxide. The proportion of pure monoetheral salt is determined by Astrac's method of titration with N/10-sulphuric acid in the presence of helianthin as indicator. Test analyses give good results.

Granulated calcium glycerophosphate should be completely soluble in five times its weight of cold, distilled water, yielding a clear solution without acid reaction. It should not give a precipitate with silver nitrate.

Calcium pyrophosphate is estimated by ignition in a muffle furnace, the temperature of which must be raised gradually. The salt may be rendered useless by the presence of mineral impurities. It is therefore preferable to determine the glycerophosphate and magnesium pyrophosphate. For this purpose, the product is fused with four times its weight of potassium nitrate, and brought in very small, successive portions into a nickel crucible heated to incandescence. The determination is completed in the manner given for calcium glycerophosphate.

Sodium glycerophosphate is analysed in much the same manner as the calcium salt. The qualitative tests are the same; moisture is determined by desiccation at 150°, and sodium pyrophosphate by

ignition. Phosphorus is estimated through the phosphomolybdate. For the estimation of sodium, the salt is converted by ignition into sodium pyrophosphate; the latter is dissolved in water, and the solution warmed until conversion into orthophosphate is complete. The latter is precipitated by addition of barium hydroxide solution in slight excess. After filtration, the solution is neutralised to sulphuric acid in the presence of litmus; the barium sulphate is removed, the filtrate evaporated to dryness, and the residual sodium sulphato weighed. Test analyses give excellent results.

The authors are led to the following conclusions. The results obtained in the analyses of pure sodium and calcium glycerophosphates by their methods (which are similar to the methods in the Codex) show these methods to be exact, and also to be applicable to commercial products. Nevertheless, determination of the residue left on calcination, of phosphorus and of metal are insufficient by themselves for the evaluation of commercial specimens. Astruc's method should also be employed for the estimation of the monothereal salt, which is the official product. The method of examination of granulated calcium glycerophosphate given in the Codex is insufficient, whilst Astruc's method loses its value on account of the presence of sugar. The content of calcium glycerophosphate can, however, be accurately determined from the estimation of phosphoric acid on the assumption that the latter is equivalent to the salt, $C_3H_5(OH)_2 \cdot PO_4Ca \cdot H_2O$.

H. W.

The Fachini-Dorta Method of (Approximately) Separating Liquid from Solid Fatty Acids in Oils and Fats. ANDREW WARKE (*Analyst*, 1914, **39**, 389-391).—The following method of applying this process was found to have advantages in respect of time over the older process. About 10 grams of the dry fat acids are placed in a flask, dissolved in 90 c.c. of anhydrous acetone, the solution is warmed to 25° , and 10 c.c. of $N\cdot 1$ per cent. hydroxide solution are added. The mixture is then cooled in ice-water for four hours, the precipitated soaps are collected on filter, washed with acetone at 0° , dissolved in warm water, and the fatty acids liberated from the solution in the usual way, dried, and weighed. The liquid acids may be separated from the acetone filtrate by adding an equal volume of water, 50 c.c. ether, and hydrochloric acid. The ethereal solution is separated, washed with water containing a small quantity of acid, is evaporated, and the residue weighed. Unless precipitation of saturated fatty acids has occurred through the employment of the drier, no diminution in the quantity of saturated fatty acids takes place when an oil is oxidised.

W. P.

The Insoluble Bromide Value of Oils. JOHN A. L. STOTT (*Analyst*, 1914, **39**, 388-389).—With regard to a method suggested by the author (*Analyst*, 1914, **39**, 28), and criticised by Ganz (this vol., ii, 681), it is mentioned that the temperature of oil before and during precipitation (11°) was stated simply to prevent formation of substituted bromine compounds. A direction to

below 5° before filtration might have been inserted; the precipitate must be washed with cooled ether, and, unless the bromides are dried are white and crumbly, the estimation is to be rejected. It is not claimed that the precipitate consists of pure hexabromide, as the method is trustworthy within a limit of 1%.

W. P. S.

Production of ω -Hydroxy-5-Methyl-2-furfuraldehyde from Carbohydrates and its Influence on the Estimation of Pentoses and Methylpentosans. MARY CUNNINGHAM and CHARLES EAST (Biochem. J., 1914, 8, 438-447).—The authors find that when 2% hydrochloric acid acts on hexoses, starch and cellulose, ω -hydroxy-5-methyl-2-furfuraldehyde is formed in amounts varying from 1 to 12%. Although it is precipitated by phloroglucinol, it does not interfere with the accuracy of pentose estimations made by the older phloroglucinol method, provided aniline acetate is used as indicator. This is accounted for on the ground of the slowness in which the ω -hydroxymethylfurfuraldehyde is produced. The suggestion of this substance, however, renders previous estimations of methylpentosans of doubtful value.

H. W. B.

Determination of Sugar in Blood. ARTHUR DUNCAN GARDNER and HENRY MACLEAN (Biochem. J., 1914, 8, 393-403).—A method is described for estimating the sugar in 2 c.c. or less of blood, involving the use of dialysed iron to precipitate the proteins and modification of Bertrand's method for the determination of the sugar in an aliquot portion of the filtrate. The results agree closely with those obtained by Bang's micro-method (this vol., ii), which takes considerably longer to carry out.

H. W. B.

New Copaiwa Balsam and Investigation of Copaiwa Balsam. D. RENZI (Chem. Zentr., 1914, i, 1886-1887; from Kiedel's Ber., 34, 27-29).—The adulteration of copaiwa balsam with so-called Indian or Ilurian balsam can be detected, according to Caesar Loretz, by an optical examination of the ethereal oil obtained in the balsam by distillation with steam. True balsams are nearly dextrorotatory, but yield a levorotatory oil and a dextro-rotatory resin. African balsam, on the contrary, is only slightly dextrally active, but yields a strongly dextrorotatory oil and an approximately equally strongly levorotatory resin.

A copaiwa balsam obtained from Amazonia, Brazil, has the following properties. It is a pale yellow, mobile, non-fluorescent oil having a normal odour and taste, and giving a turbidity in an equal volume, and a white precipitate with an excess, of white alcohol. It has $D^{15} 0.930$, saponification number 23.8, α^{20} value 42.1, $\alpha^{20} - 40^\circ$, and contains 20.4% of resin ($\alpha^{20} - 55^\circ$); the ethereal oil has $\alpha^{20} - 35.920^\circ$.

C. S.

Detection of Saponin in Beverages. NAZARETH CAMPOS (Ann. Inst. med., 1914, 19, 289-293).—The beverage is neutralised with ammonium carbonate, concentrated, and extracted with phenol; a phenol solution is then shaken with ether and water, the

saponin being thus obtained in aqueous solution. Substances other than saponin, however, also pass into the aqueous solution and interfere with the tests which are applied to the residue, obtained on evaporation, in order to identify it as saponin. The solution is, therefore, evaporated to 25 c.c. and shaken with 125 c.c. of saturated barium hydroxide solution; a compound of saponin and barium hydroxide is precipitated. After the liquid has been decanted, the precipitate is decomposed with carbon dioxide, the barium carbonate is separated by filtration, and the filtrate evaporated to dryness. The residue obtained, consisting of saponin mixed with barium carbonate, is extracted several times with 95% alcohol, and the alcoholic solutions are evaporated separately. The first extract may contain a quantity of colouring matter, but the subsequent solutions yield pure saponin on evaporation. The sulphuric acid test is recommended for identifying the saponin. The reaction with Nessler's reagent, described by Vamvakas (1906, ii, 504), is untrustworthy, since a number of materials, particularly coffee extract, yield substances giving reactions which cannot be distinguished from that given by saponin. W. P. S.

Defecation of Urine by Acid Mercury Nitrate. CHI LONG (J. Pharm. Chim., 1914, [vii], 9, 602).—In a recent communication by Berner (this vol., ii, 587), the use of mercury nitrate for the defecation of urine is ascribed to Patein and Dufau. The author points out that this reagent was first employed by him, and his priority has been recognised by Patein and Dufau. H. W.

[**Estimation of Allantoin.**] MAURICE H. GIVENS (J. Biol. Chem., 1914, 18, 417–424).—See this vol., i, 1144.

The Determination of the Lime Requirements of the Soil. H. B. HUTCHINSON and K. MACLENNAN (Chem. News, 1914, 112, 61–62).—A brief review of methods previously suggested for the estimation of the lime requirements, or acidity, of the soil. Most of these are purely qualitative, while the quantitative methods are largely based on reactions having no relation to those obtaining in the field.

The one proposed by the authors consists in the treatment of the soil with an *N*/50 solution of calcium hydrogen carbonate for three hours, under constant agitation. The soil suspension is then filtered, an aliquot portion of the filtrate titrated with *N*/1000 potassium hydroxide using methylorange as indicator, and the amount of alkali absorbed is then calculated. Usually, 10–20 grams of soil, and 200–300 c.c. of solution, are taken for field soils, but these values must be adjusted so that the concentration of the final hydroxide solution is not less than approximately *N*/100 strong. H. B. H.

